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# TRANSACTIONS

OF THE

## AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS

(INCORPORATED)

Vol. 117

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## INSTITUTE OF METALS DIVISION 1935

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PAPERS AND DISCUSSIONS PRESENTED BEFORE THE DIVISION AT MEETINGS HELD  
AT NEW YORK, OCTOBER, 1934 AND FEBRUARY, 1935 AND  
AT CHICAGO, OCTOBER, 1935

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## *Notice*

This volume is the ninth of a series constituting the official proceedings of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers. It deals with nonferrous metals and includes papers presented at the New York Meeting, Oct. 2-4, 1934, the New York Meeting, Feb. 18-21 and the Chicago Meeting, Oct. 1-3, 1935.

The series is a continuation of the publications and proceedings of the Institute of Metals Division. The complete list of publications and proceedings, including the present volume, is as follows:

1908-1911 *Transactions of the American Brass Founders' Association*: 1908, Vols. 1 and 2; 1909, Vol. 3; 1910, Vol. 4; 1911, Vol. 5.

1912-1916 *Transactions of the American Institute of Metals*, Vols. 6-10.

1917-1918 *Journal of the American Institute of Metals*, Vols. 11-12.

1919-1926 *TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers*, Volumes 60, 64, 67, 68, 69, 70, 71 and 73.

1927-1928 *PROCEEDINGS of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers*, two volumes, of which the later is now designated Vol. 78 of the A. I. M. E. *TRANSACTIONS*.

1929-1935 *TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers*, Volumes 83, 89, 93, 99, 104, 111 and 117, Institute of Metals Division.

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## FOREWORD

THIS volume contains papers presented at the October, 1934, meeting in New York, the February, 1935, meeting in New York and the October, 1935, meeting in Chicago. The annual Institute of Metals Division lecture, presented by Dr. C. A. Edwards on "Gases in Metals" as one of the features of the program in New York in February, is also published herewith.

In reviewing events of the year that are of importance to I.M.D. members, mention must be made of the publication of "Modern Uses of Nonferrous Metals" for the Seeley W. Mudd Fund by the American Institute of Mining and Metallurgical Engineers. Dr. C. H. Mathewson, one of our past chairmen, edited this volume and many of the chapters were written by our members.

Of interest, also, to all members of the Division, especially authors of papers, is the Annual Award Certificate that was established two years ago. The conditions of award and the titles of the two papers so far chosen for this award, with authors' names, are listed on page 10 of this volume.

It is customary for the chairman to avail himself of this medium for expressing his appreciation to the committee chairmen and officers who have assisted in the work of the Division during the year. The present chairman feels that besides the excellent work of the Papers and Publications Committee under Dr. Mehl, which is witnessed by this volume, the constructive interest and activity of the Executive Committee of the Division has been unusual and augurs well for the future of the Division.

W. M. PEIRCE, *Chairman*,  
Institute of Metals Division.

PALMERTON, PA.,  
October 25, 1935.



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## THE INSTITUTE OF METALS LECTURE

AN annual lectureship was established in 1921 by the Institute of Metals Division, which has come to be one of the important functions of the Annual Meeting of the Institute. In 1934 the Division established the custom of presenting a certificate to each lecturer.

A number of distinguished men from this country and abroad have served in this lectureship. The roll is quoted below:

- 1922 Colloid Chemistry and Metallurgy. By Wilder D. Bancroft.
- 1923 Solid Solution. By Walter Rosenhain.
- 1924 The Trend in the Science of Metals. By Zay Jeffries.
- 1925 Action of Hot Wall: a Factor of Fundamental Influence on the Rapid Corrosion of Water Tubes and Related to the Segregation in Hot Metals. By Carl Benedicks.
- 1926 The Relation between Metallurgy and Atomic Structure. By Paul D. Foote.
- 1927 Growth of Metallic Crystals. By Cecil H. Desch.
- 1928 Twinning in Metals. By C. H. Mathewson.
- 1929 The Passivity of Metals, and Its Relation to Problems of Corrosion. By Ulck R. Evans.
- 1930 Hard Metal Carbides and Cemented Tungsten Carbide. By S. L. Hoyt.
- 1931 X-ray Determination of Alloy Equilibrium Diagrams. By Arne Westgren.
- 1932 The Age-hardening of Metals. By Paul D. Merica.
- 1933 Present-day Problems in Theoretical Metallurgy. By Georg Masing.
- 1934 Ferromagnetism in Metallic Crystals. By L. W. McKeehan.
- 1935 Gases in Metals. By C. A. Edwards.

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## ANNUAL AWARD CERTIFICATE OF THE INSTITUTE OF METALS DIVISION

In 1933, the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers established its annual award of an engraved certificate to the author or authors of the paper that in the opinion of the award committee represents the most notable contribution to metallurgical science among the papers that have been accepted by the Division for presentation at one of its meetings and have been published by the Institute within the three years preceding the date of award. The award is made by the Division each February.

There are no restrictions with respect to nationality, age or occupation of the author or authors.

Awards have been made as follows:

- 1934 Robert F. Mehl and Charles S. Barrett: Studies upon the Widmānstätten Structure, I—Introduction. The Aluminum-silver System and the Copper-silicon System. *TRANSACTIONS* (1931) **93**, 78-110.
- 1935 E. A. Anderson, M. L. Fuller, R. L. Wilcox and J. L. Rodda: The High-zinc Region of the Copper-zinc Phase Equilibrium Diagram. *TRANSACTIONS* (1934) **111**, 264-292.





C. A. EDWARDS

*Institute of Metals Division Lecturer, 1935*

## Gases in Metals

By C. A. EDWARDS\*

(Institute of Metals Division Lecture†)

LONG before metals and their alloys were regarded as belonging to a special branch of physical chemistry and studied in the light of physico-chemical laws, in some sections of the metalliferous arts it was recognized that their behavior and properties could be affected by gases which they might take up during refining or melting operations.

Quite a good example of this is to be found in copper refining. The early workers of copper must have been acquainted with the fact that this metal was peculiarly sensitive to the influence of gases, for they knew the conditions that were necessary for the production of "tough-pitch" copper, which is so intimately bound up with the gas or gases the metal contains prior to casting. Another instance, which must have been known at least superficially, is that of silver. For this metal, when molten, will absorb large volumes of oxygen from the atmosphere and, if proper precautions are not taken to prevent this absorption, unsound castings or ingots are obtained when the metal is cast. The well-known spitting of silver, while solidifying, is due to the liberation of this gas.

Speaking generally, however, and looking at the subject of gases and metals from a scientific point of view, the knowledge early workers possessed must have been scanty and of a rather speculative character, for it is only during comparatively recent years that anything approaching reliable information has been available.

The position is much the same with regard to the other metals and their alloys, which are known to take up gases when they are in either the liquid or solid state. In other words, we are only beginning to get the necessary evidence which enables us to appreciate how important this subject is, and how fascinating it has become.

It is true that some metals, such as tin and lead, etc., do not display a marked, if any, tendency to absorb gases; and, so far as we are at present aware, they are not seriously affected by any gas or gases they might be capable of holding in solution.

The systematic study of the behavior of metals towards different gases presents many special experimental difficulties; and, in many

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\* Principal, University College of Swansea, Wales.

† Presented at the New York Meeting, February, 1935. Fourteenth annual lecture. Manuscript received at the office of the Institute Feb. 18, 1935.



instances, it is far from easy to draw reliable conclusions from the evidence obtained. This is especially pronounced when dealing with high temperatures and complex mixtures of gases which are capable of giving rise to secondary reactions.

It is mainly because of these reasons that the rate of progress with regard to the accumulation of trustworthy data in this field of study, and their correct interpretation, has been so slow.

There are numerous angles from which this subject can be studied, and each is of considerable interest. They all have some bearing upon the physical and mechanical properties of one or other of the metals or alloys that are in daily use.

In some instances, the influence of changing temperature upon the degree of solubility of a gas, especially at temperatures where there is a change of state, as from liquid to solid, produces a deleterious effect upon the internal character of an ingot or casting.

Then again, some metals under certain conditions readily absorb a gas even at temperatures well below their melting points; and, when this occurs, it frequently produces a direct and drastic modification in the properties of the metal; similar changes may be produced between a newly absorbed gas and some other element or compound previously present in the metal.

Before attempting to discuss this matter in detail, it will be useful at this stage to give a brief outline of the four main conditions in which gases may be associated with metals. They are as follows: (1) adsorbed gases, (2) dissolved gases, (3) gases in chemical combination, (4) gases entrapped in blowholes, or cavities.

Adsorption is essentially a surface phenomenon. In general, and even in the case of metals, this phase of the subject more naturally belongs to physics and chemistry than to metallurgy. However, the facts that have been discovered concerning the behavior of adsorbed films of gas on metallic surfaces are of such a fundamental character, and the deductions that have been drawn from them are so important, that they form one of the most suitable bases on which to build a discussion of the more general subject.

The behavior of adsorbed films has been studied by many investigators; but the most important researches, at least for our present point of view, are those by Dr. I. Langmuir<sup>1</sup>.\*

In discussing the effects of adsorbed films of oxygen on tungsten filaments, in relation to hydrogen, he said:

Thus, if a mixture of oxygen and hydrogen be introduced into a bulb, and the filament heated to 1500° C., instead of the gases reacting to form water vapor, as they would in contact with a platinum filament, the oxygen reacts gradually with

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\* References are at the end of the paper.

the tungsten to form  $\text{WO}_3$ . While this is going on the dissociation of the hydrogen by the filament is entirely prevented so that, finally, nearly pure hydrogen remains, and the pressure becomes constant. After 10 or 15 minutes, the pressure of the oxygen decreases to such a point (a minute fraction of one bar) that it is no longer able to prevent the dissociation of the hydrogen. This, then, begins suddenly to dissociate, and in a few minutes more all of the hydrogen has disappeared. The oxygen films on the tungsten surface thus consist of oxygen in a form which cannot react with hydrogen, even at  $1500^\circ \text{C}$ . . . .

The remarkable stability of these oxygen films, as well as the complete change in the chemical properties of the oxygen, give reason for believing that the atoms are chemically combined with the underlying tungsten atoms. This film cannot be regarded as consisting of ordinary oxide of tungsten, nor as atomic oxygen. The oxygen atoms are probably held to the surface by electrons, just as the oxygen atoms are held to the carbon atom in  $\text{CO}_2$ . The oxygen atom is thus chemically satisfied, but the tungsten atoms are not saturated, so that they are held by strong forces to the tungsten atoms that lie below them.

Thus, "every atom within a solid is tied up to an equilibrium point within a space lattice; but they are also attached to all neighboring atoms by primary or secondary valency." Hence, a crystal constitutes a single large molecule held together by chemical forces. The layer of atoms constituting the surface would thus present unbalanced and unsatisfied valencies on their outer side.

Adsorption, therefore, is regarded as being the attachment of outside molecules or atoms to the exposed free valencies of the atoms comprising the surface layers.

In many instances, where adsorbed films of gas are formed on metallic surfaces, this is accompanied by a process of diffusion of the gas into the metal itself. This has been discussed by Andrew and Holt<sup>2</sup>, and others, for palladium and platinum, with hydrogen.

Another instance of a similar kind is found in iron and hydrogen. When this gas is developed on the surface of iron (either by acid attack or by electrolysis), the gas is first adsorbed on the surface and then diffuses through the metal, even at the ordinary temperature. The rate of this diffusion increases with the rate at which the gas is generated on the surface of the metal<sup>3</sup>.

It has been suggested by some writers that diffusion of a gas through a solid metal occurs by almost exclusively passing through the material at the crystal boundaries. In other words, this transportation of the gas was thought to go on only through the amorphous cement which was supposed to exist at boundaries of a multicrystal metallic mass.

It does not seem necessary to make this assumption to envisage the diffusion of a gas through a solid metal. It is well known that solid elements will readily diffuse through a crystalline metal; and there is every reason for considering that gases will obey the same law.

It is true that in instances where we can clearly study gaseous diffusion, we notice that the speed of transportation is so much more

rapid than with solid elements; but, after a little consideration this is not surprising.

In the first place, it is obviously impossible for gaseous molecular diffusion to take place. If we accept Langmuir's evidence that an adsorbed film is a special form of chemical combination of the gas with the surface atoms of the metal, then when this is followed by diffusion the volume of the hydrogen atoms under these conditions is so small as to present comparatively little resistance to its passage through the space-lattice of the crystal. Whereas, in the case of the diffusion of most solid elements into metallic crystals, this is brought about by a process of atomic displacement, or substitution.

However, all doubt concerning the possibility of a gas diffusing through the body of a crystal was removed by an experiment I made some time ago, in which it was found that no difference could be detected between the rate at which hydrogen diffused through a single crystal of iron, and through the same material after it had been recrystallized into a mass of small crystals.

What I have just said must not be taken to mean that I am suggesting that there cannot be a somewhat greater concentration of gas at the boundaries of adjacent crystals; nor does it mean that the effect of a gas must be the same at the boundaries as when it is within the body of the crystals. Indeed, there is evidence to show that hydrogen, under certain conditions, will render iron very brittle at the crystal boundaries.

This was very clearly demonstrated by Pfeil<sup>4</sup> when experimenting with samples of almost pure iron containing crystals of about 1 in. in diameter. He found that when such a specimen had been pickled for 30 minutes in 20 per cent sulfuric acid the crystals could be broken away from each other at the crystal boundaries.

It is interesting to note that the brittleness at the crystal boundaries was so marked that fracture was produced without any substantial deformation in the body of the crystals themselves.

It may be useful to consider the above facts in greater detail, for as they stand they might be taken as an indication of the existence of the so-called amorphous cement at the crystal boundaries. This conclusion should not be drawn without some qualification, or attempt to give a definition of the meaning of the term "amorphous cement."

In this connection, it is, perhaps, necessary to remember that in the "amorphous cement" theory, as originally put forward, it was postulated that films of uncrystallized material (i.e., supercooled liquid) existed between the crystals. Further, it was supposed that these films were relatively very thick, as compared with the atomic dimensions of the metal.

When viewed in the light of recent knowledge concerning the space-lattice structure of crystals, I find it impossible to imagine how such

supercooled films could exist. The difficulty disappears if we simply consider that the atoms, at and near the crystal boundaries, lie in positions that are somewhat distorted from the normal space-lattice by the pull that is exercised upon them by the atoms immediately across the boundary of adjacent crystals. The degree of this distortion will, of course, quickly diminish as the distance of the atoms from the boundary increases.

The object of the above remarks is intended as a criticism of the use of the term "amorphous," which seems to have been a particularly unfortunate one, and in many ways misleading.

Some of the atoms at and near the crystal boundaries will have unsaturated bonds, and in consequence of this there will be a rather greater concentration of the gas in those parts than in the main body of the crystals. This will give rise to an increased degree of distortion of the space-lattice, and thus lead to an intensified influence of the gas as a result of greater internal stresses being set up.

It is interesting to note, at this stage, that Phelps<sup>5</sup> has shown that what must be regarded as very small quantities of hydrogen in gold (say, about 0.02 to 0.04 per 1000), which may be taken up when the metal is melted in an atmosphere of that gas, affects the behavior of the metal in two ways:

1. After gold is melted under hydrogen there is no sign of shrinkage on casting; whereas, after melting in air, there is a distinct "pipe."
2. This hydrogen treatment raises the temperature at which cold-work hardening is removed from 150° C. to 300° C.

Many researches have been undertaken by a large number of investigators concerning the temperature and conditions under which dissolved hydrogen, in particular, can be at least partially removed from different metals. For the present purpose it is quite unnecessary to refer to these in detail. The case of iron and hydrogen, however, presents so many features of interest that it will serve as a useful general example for purposes of discussion.

It has long been known that hydrogen which has diffused into iron, as a result of acid attack by pickling, or by electrolytic deposition of the gas upon the metal, is partly removed by exposing the metal to the atmosphere at the ordinary temperature. Further, considerably more can be eliminated by raising the temperature, and even greater quantities by jointly raising the temperature and reducing the pressure.

The deleterious effects of excessive amounts of hydrogen dissolved in, or associated with, iron can be completely removed by annealing at suitable temperatures.

This is rather clearly illustrated by the data plotted in Fig. 1. This curve represents the Erichsen values obtained for electrolytic iron sheets, after annealing at temperatures between 250° and 950° C. From this,

it will be seen that the hydrogen brittleness associated with electrolytic iron is rapidly diminished at about 250° C., and seems to be almost entirely removed after a short annealing at a temperature of about 700° C. The change in the properties is accompanied by a recrystallization of the metal, similar to that which takes place during the annealing of heavily cold-rolled material.

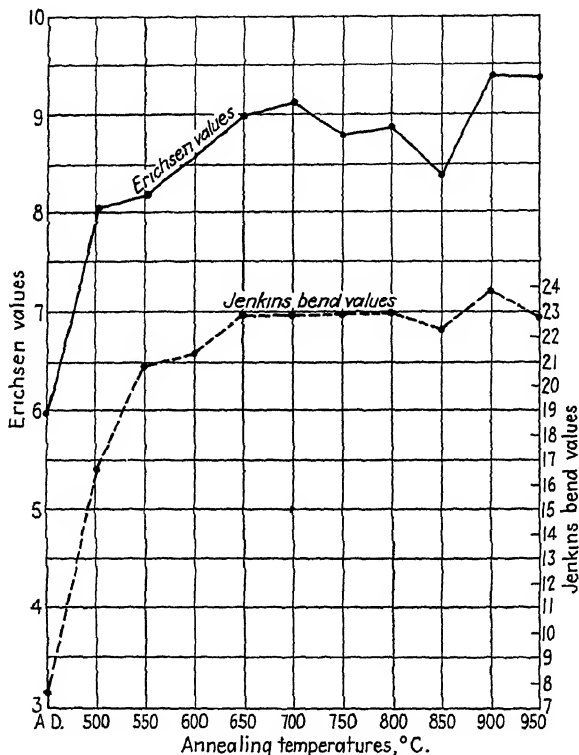


FIG. 1.—ERICHSEN AND JENKINS BEND VALUES OF ELECTROLYTICALLY DEPOSITED IRON SHEETS 82 MM. THICK.

While there is every reason to believe that a considerable proportion of the hydrogen originally associated with the deposited iron is eliminated by annealing at moderate temperatures, it is extremely difficult to remove the last traces. Indeed, it is questionable whether iron from which the last trace of hydrogen has been extracted has ever been examined.

The primary object of referring to this is to emphasize what might be described as an appeal made a few years ago by T. D. Yensen<sup>6</sup> for a concerted attempt to study the properties of absolutely pure iron, more particularly with the view of ascertaining whether the  $A_3$  and  $A_4$  changes are, in some way, due to the disturbing effects of such elements as hydrogen, carbon, oxygen, phosphorus, and so forth.

A short quotation from one of Yensen's papers will be useful at this stage. In discussing the classification of the elements in relation to their influence upon iron in this connection, he says:

It seems more logical to classify the elements on the basis of the position they occupy in the space lattice. The atoms of one class to which nickel, silicon, etc., belong, take the place of iron atoms in the lattice structure, and explain their high solubility; they are substitution atoms. The atoms of the other class, on the other hand (to which carbon, oxygen, phosphorus, etc., belong when they are dissolved in iron), seem to occupy the interstitial space between the iron atoms and account for their low solubility; they are interstitial atoms.

The substitution atoms can enter the iron lattice in relatively large numbers, without radically changing the characteristics of the iron. When we add 1 per cent silicon to iron, we make it somewhat harder and increase the electrical resistance; but the magnetic characteristics are very little changed.

The interstitial atoms, in entering the lattice in even very small numbers, create a strained condition, and there is a tendency for the lattice to change from a body-centered cube to the face-centered cube, in which the solubility is far greater.

It is the elimination of the interstitial elements from iron that is of greatest importance, in order to obtain the physical characteristics of pure iron. We are not greatly concerned about 0.01 per cent of nickel or silicon, but the same amount of carbon or oxygen in solution produces large effects.

These are extremely interesting observations, which should be given careful consideration. Many years ago, I repeatedly attempted to get evidence bearing upon this problem; but, until Yensen's views were published, the only element I had in mind (as regards the A<sub>3</sub> point) was hydrogen.

It is to be hoped that the negative results so far obtained will not discourage further efforts. It should be remembered that, as Yensen has already indicated, special precautions must be taken in order to prepare iron that is entirely free from the elements mentioned above. Possibly one hopeful line of pursuit would be to melt samples of electrolytic iron in an atmosphere of hydrogen, and after keeping it molten under these conditions for some time with the object of eliminating oxygen and carbon, to subsequently displace any hydrogen by means of an inert gas, such as argon. The elimination of the last trace of hydrogen might require prolonged heating well above the melting point of the metal.

#### DEFECTS DEVELOPED BY THE DIFFUSION OF HYDROGEN IN METALS

Let us now turn to a brief consideration of two well-known defects which hydrogen causes when it diffuses into solid copper, on the one hand, and into iron or mild steel, on the other.

In some respects, the conditions to be considered under which hydrogen diffuses into these metals are quite different. When specimens of

copper which contain free oxide of copper are annealed at a red heat in a strongly reducing atmosphere containing appreciable amounts of hydrogen, the metal becomes what is generally known as "gassed." This is caused by hydrogen dissolving in the metal and, as it diffuses and comes into contact with the free oxide of copper, the latter gets reduced, with the formation of water vapor. At the annealing temperatures, this water vapor, which mostly becomes located at the crystal boundaries, causes a partial rupture at the crystal boundaries and the metal is thereby rendered brittle.

During the pickling of iron or mild steel, hydrogen freely diffuses into the metal, even at the ordinary atmospheric temperature, and this also occurs when the gas is electrolytically deposited upon such surfaces. Further, it is known that, if the necessary precautions are taken to confine this action to one surface of the material, the gas can be collected on the other side. When, however, there are nonmetallic impurities present, such as, say, oxide of iron or slag inclusions, straightforward diffusion of the hydrogen is interfered with. Under these conditions there is a distinct tendency for the hydrogen as it diffuses to the boundary walls of the inclusions to accumulate in the molecular condition, and develop enormous internal pressures causing blisters.

When dealing with thin material, these blisters may become externally evident, especially if the temperature is subsequently raised to a moderate extent. So far as I am aware, these phenomena do not occur at the boundary walls of cementite, possibly because this constituent is, shall we say, wetted by the ferrite surrounding it. In these circumstances, the concentration of the hydrogen associated with the atoms of iron around the cementite reaches a figure which is appropriate to the rate of its formation on the outer surface, but cannot get liberated in the molecular condition and overcome the cohesion at the interface of the two constituents.

It is different in the case of oxide of iron. In this substance, the accumulation of molecular hydrogen might be regarded as commencing in one of the following ways:

1. The hydrogen might reduce a small quantity of one of the lower oxides of iron in contact with the ferrite, and the molecules of water so formed give the necessary discontinuity for additional hydrogen to accumulate.

2. There may be fissures in the oxide of iron which provide the necessary space for the first molecules of hydrogen to collect.

3. The tendency for dissolved hydrogen to form the insoluble molecules of the gas may itself be great enough to overcome the rather slight cohesion that exists between oxide of iron and ferrite.

When the blisters that can be formed in this way are considered, it is evident that the internal pressures must be extraordinarily high.

INFLUENCE OF TEMPERATURE AND PRESSURE UPON THE  
SOLUBILITY OF GASES IN METALS

In considering the influence of temperature upon the extent to which gases may be retained in association with metals, care is necessary to define the conditions under which the observations have been made. For example, when metals have been electrolytically deposited from aqueous solutions, they are liable to have an excessive amount of hydrogen deposited with and retained by them. This is particularly evident in the case of copper and iron.

It must not be assumed that anything like the whole of this hydrogen is in a state that can be correctly described as being in solution. Under these conditions, it would be unwise to attempt to give a precise definition of the state in which the gas exists. Some is dissolved, but a large proportion must be present in a condition bordering between "adsorbed" and "entrapped" films. In whatever form it exists, the amount present is considerably in excess of that which can be properly held in solution by the metal. This is proved by the fact that large quantities of hydrogen can be eliminated from electrolytic iron and copper, by annealing at comparatively low temperatures. It must not be assumed from this, however, that the real solubility is decreased by raising the temperature. It simply means that the higher temperatures increase the facility with which the excess of gas present is removed and equilibrium attained.

Many investigators have made a study of the quantity and nature of the gases which are to be found in commercial metals and alloys, and many useful data have been accumulated. A large proportion of these, however, relate to samples of material that have been prepared commercially, when the influence of more than one gas has been present and the conditions have not been under satisfactory scientific control. This has often made it difficult, and sometimes impossible, to draw accurate conclusions from the results obtained.

Reliable evidence, however, has<sup>7</sup> been obtained by Sieverts<sup>1</sup>, whose investigations have covered a study of the solubilities of gases in metals over wide ranges of temperature up to and, indeed, exceeding the melting points of a large number of metals. It is unnecessary to describe his results in detail, but there is one fact with regard to the influence of pressure, which stands out very prominently as a result of his work.

He found that the amount of gas capable of being held in solution by a given metal at a constant temperature was proportional to the square root of the pressure of a single gas. In the case of a mixed gas, the quantity of any one of them dissolved in the metal is proportional to the square root of its partial pressure. Hence, by diluting the concentration of a given gas in contact with a liquid metal while the pressure is kept constant, the amount of that gas dissolved in the metal will



diminish as a new state of equilibrium is established. Changes of this kind are not instantaneous; that is, equilibrium is not necessarily attained immediately; and, in some instances, considerable time is required for it to be achieved. Among other factors, the rate of the change will depend upon the ratio of exposed surface area to the mass of metal, and the speed with which the liberated gas is removed from the surface of the metals.

It will be seen from the above observations, concerning the influence of pressure, that great caution must be exercised before drawing conclusions from analyses of the gas content of blowholes, as to the primary cause of the formation of such holes or cavities. If, for example, the gas contained in a blowhole was found to be largely composed of hydrogen, carbon monoxide and nitrogen, with traces of moisture, it would not follow that any one of the three gases named initially gave rise to the hole; it might have been caused by the moisture. In this event, the cavity once having been formed and the partial pressure of the other gases being zero, a liberation of the gases dissolved in the metal would take place, and, finally, the quantity in the whole might exceed the original volume of moisture present.

### BLOWHOLES

This question of the formation of blowholes during the casting of metals, and the factors that control the positions in which they can be located in ingots or any other form of casting, is full of theoretical interest and practical importance.

It is clearly associated with the marked change in the solubility of a gas or gases, which so frequently accompanies a transformation from the liquid to the solid state, or to chemical reactions which might occur during the progress of solidification. Reactions of the latter kind, which give rise to the formation and liberation of a gas, can sometimes occur between elements already present in the liquid prior to the operation of casting, or the gas may be formed by reactions between the element dissolved in the liquid (such as carbon or hydrogen) and the oxygen of the atmosphere with which it comes into contact during the process of casting.

In practically all instances where the changing degree of solubility of a gas in a metal has been studied, it has been found that the most pronounced alteration in the solubility occurs at temperatures that correspond to the melting points of the respective metals. The change is of such a nature as to indicate a marked increase in the amount of gas which can be dissolved in the metal as it passes from the solid to the liquid state.

With the exception of silver and oxygen, the solubility increases as the temperature is raised above the melting point; but, with silver, which

can dissolve twenty-three times its own volume of oxygen at N.T.P., there is a clearly defined decrease with rising temperature. The difference in this respect is usually ascribed as being due to the formation of a silver oxide  $\text{Ag}_2\text{O}$  that is less stable at high temperatures and, therefore, the curve is not a normal solubility curve, but a dissociation curve. The abrupt change in the solubility at the melting point is considered to be due to the oxide being entirely unstable in the solid state.

It will be remembered that I have already suggested there are four main conditions in which gases may be associated with metals; i.e., (1) adsorbed, (2) dissolved, (3) gases in chemical combination, (4) gases entrapped in cavities.

We have already seen from Langmuir's views that, in regard to adsorbed films of gas on solid metals, we are really dealing with a special type of chemical combination. The cases falling in group No. 4, we need not discuss, for in whatever form the gases might have been prior to their liberation in the form of blowholes, they are not in chemical combination with the metal once they enter a blowhole.

With regard to Nos. 2 and 3, however, there is some uncertainty as to whether the presence of a gas, especially in a liquid state, should be regarded as being simply in "solution," or in "chemical combination." With metals such as copper, iron or silver, with, say, oxygen, there is no objection to the view that these metals, when liquid, can dissolve their respective oxides.

When dealing with a gas like hydrogen and liquid copper, iron, nickel, etc., the position is not so simple. The only point we can make with any degree of certainty, in this connection, is that the gas is not present in the molecular state; and, since we have no evidence which definitely points to the existence of hydrides of these metals at very high temperatures, it will be better, in the present state of knowledge, to consider cases of this kind as being "solutions."

The example of silver and oxygen will serve as a useful instance of how the amount of gas contained in the liquid metal might affect the internal character of a cast ingot. In this case, we are simply dealing with a change in the solubility of the gas during solidification, without being confused by the possibility of supplementary reactions arising from the action of the atmosphere and the liberated oxygen, or by secondary reactions between that gas and impurities contained in the liquid silver.

The melting-point diagram of the silver-oxygen system is of the simple eutectic type, and is qualitatively illustrated in Fig. 2. This indicates that as freezing proceeds at temperatures of the line  $AC$ , crystals of silver are formed which hold no oxygen in solution; and, if the rate of cooling is slow enough to permit of equilibrium being established, there will be a progressive concentration of the oxygen initially contained in

the original liquid in a steadily decreasing amount of residual liquid silver. Finally, at the temperature immediately above the line  $BC$ , the remaining liquid will contain  $C$  oxygen.

As previously mentioned, the quantity of oxygen capable of being held in liquid silver diminishes with rising temperature; it follows that, if the surfaces of two separate batches of pure silver are freely exposed to the atmosphere, at widely different temperatures, the amount of

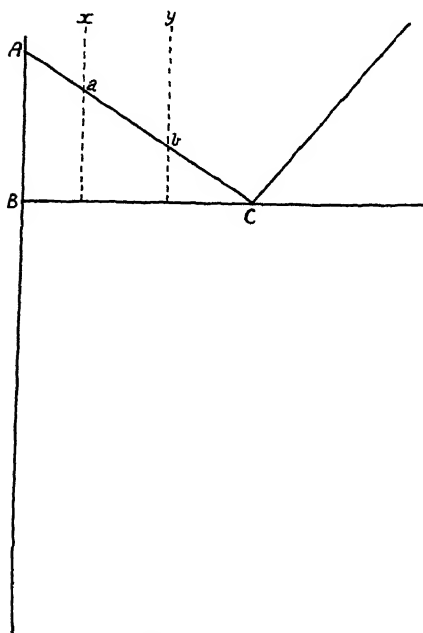


FIG. 2.—MELTING-POINT DIAGRAM OF SILVER-OXYGEN SYSTEM, QUALITATIVELY ILLUSTRATED.

oxygen they contain will be less the higher the temperature.

Let us now follow what is likely to take place during the solidification of two such samples, after casting. That which was kept at the higher temperature would contain a relatively small quantity of oxygen, say  $x$ , Fig. 2; and would, on cooling to  $a$ , begin to deposit solid crystals which would grow on the walls of the mold. Now, providing the cooling rate was not too quick to permit of equilibrium being maintained, as cooling proceeded, there would be no liberation of oxygen during the early stages of freezing, but merely a concentration of that gas in the residual liquid until the temperature of the line  $BC$  was reached. At that temperature, however, oxygen would be freely liberated as solidi-

fication proceeded; and this would partly escape through the upper surface of the ingot, but some would get entrapped in the form of blowholes.

It will thus be seen that the thickness of the solid rim or shell of the ingot must depend upon the extent to which crystallization proceeds, as the temperature falls to that of the line  $BC$ , when the oxygen concentration in the liquid has reached that of  $C$ , when liberation of oxygen commences.

In the sample that was maintained at the lower temperature, and which would be more highly charged with oxygen, previous to casting, the liberation of oxygen after casting would begin at an earlier stage than the sample just considered; and, therefore, a thinner solid shell, or rim, would be formed.

It should be mentioned that, even when dealing with such a simple example as silver and oxygen, where we can assume no secondary reac-

tions come into play, it might be impossible to predict, even approximately, what the thickness of the solid rim would be without having reliable information concerning the rate at which oxygen can diffuse in liquid silver. That is to say, we would need to know the rate at which the concentrated solutions of oxygen in silver formed at the interfaces of the liquid and solid phases would diffuse into the less highly concentrated portions of the liquid. If there happened to be a material lag in this, the liberation of oxygen would occur at an earlier stage than would be anticipated from theoretical considerations based on the assumption that equilibrium is coincident with solidification; and, further, this tendency would be emphasized by anything that causes an acceleration in the rate of solidification.

In general, we may say that the principal factors that increase the rate of crystallization, after casting, are low casting temperature, reduction in the size or mass of the casting, increases in the wall thickness of the ingot molds, and greater thermal conductivity of the mold material.

In the case just considered, we have been dealing with the simplest instance of the effect of the liberation of gas during solidification of a metal arising from a marked decrease of solubility resulting from this change of state.

In many instances, however, owing to the presence of a third element, secondary chemical reactions develop during solidification. When this occurs, it is much more difficult to follow their effects in detail, especially when it is desired to indicate the stage at which blowholes might be formed during the solidification of an ingot.

A useful qualitative example of this kind can be found in copper and hydrogen. It is known that, although the solubility of hydrogen in solid copper immediately below the melting point is less than when just above that temperature, the amount of hydrogen which can be dissolved in the solid metal is appreciable.

Starting with liquid copper, containing a smaller quantity of hydrogen in solution than is capable of being dissolved by the corresponding solid metal and not considering the possibility of gaseous segregation, there should be no tendency for the liberation of gas and the formation of blowholes during solidification. Under these conditions, it is possible to produce solid copper free from blowholes providing the necessary precautions are taken to protect the metal from being contaminated with oxygen before and during solidification. This can be done by protecting the surface of the liquid by means of a layer of charcoal, and allowing it to solidify in the crucible; or, in a somewhat less effective manner, by melting under and keeping a layer of charcoal on the metal up to the moment of casting. If, however, precautions are not taken to prevent the hydrogen contained in the metal from reacting with oxygen, then blowholes are developed.

The effects of oxygen reacting with hydrogen dissolved in copper can be prevented by chemical means; for example, by the addition of small quantities of phosphorus which will combine with the oxygen that would otherwise be taken up by the molten copper. The chief point I wish to stress, in this connection, is that even when the amount of a gas present in a liquid metal may be much too small of itself to give rise to blowholes in a casting, it may, indirectly, produce unsoundness by reacting with other elements. In the case of oxygen, this may be already dissolved in the liquid, or it may be taken up during casting.

There is ample evidence in support of the view that oxygen and hydrogen can co-exist in solution with liquid copper. This simply means that there is a tendency for the reaction  $2\text{H}_2 + \text{O}_2 \rightleftharpoons \text{H}_2\text{O}$  to move from right to left in the presence of liquid copper. In all probability, this tendency increases as the concentration of the hydrogen and oxygen diminishes. Some indication of this and, incidentally, of the difficulty of removing dissolved hydrogen from liquid copper is revealed from a consideration of the following experiments, which were made by Prytherch and Edwards.

Ten pounds of cathode copper were melted in a clay-lined Salaamander crucible, and then cast. The density of the ingot was found to be 8.07. This low figure may be considered to be due to the hydrogen present in the metal reacting with the oxygen taken up during casting. Successive casts from the same kind of original copper were then made, as follows:

Four different lots of molten copper were heated to a temperature of  $1150^\circ \text{C}$ ., when various quantities of  $\text{Cu}_2\text{O}$  were added to the different melts. Each melt was then allowed to stand for twenty minutes to enable the oxide to become completely dissolved, and give it an opportunity of reacting with the hydrogen present. Charcoal was then added, and sufficient time allowed for the reduction of the remaining oxide, and the metal was then cast. As would be expected, it was found that the density of the ingot was proportional to the weight of copper oxide added:

No.	OXYGEN, PER CENT	DENSITY
1	0	8.07
2	0.5	8.27
3	1.25	8.36
4	2.0	8.56

One of the most striking features concerning these and other experiments was the large quantity of oxygen required for the oxidation of relatively small quantities of hydrogen, the weight of oxygen being many times greater than should be necessary, according to the equation  $2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}$ .

The time factor cannot be neglected. But, as will be seen later, this cannot have had a serious effect upon the results just referred to.

A series of melts were made in every way similar to those already mentioned, with the exception that 0.25 per cent of oxygen (in the form of  $\text{Cu}_2\text{O}$ ) was added in each case, and the metal allowed to stand for predetermined times at  $1150^\circ \text{C}$ . After reduction of the oxide, in the usual manner, casting was proceeded with and the following results were obtained:

No.	TIME OF OXIDATION, MIN.	DENSITY
1a	0	7.94
2a	15	8.09
3a	30	8.10
4a	45	8.14

With low concentrations of hydrogen practically no water vapor is produced until the cooling reaches solidifying temperature. At this temperature, however, water vapor is formed and becomes entrapped in the semi-pasty mass in the form of blowholes. The reaction between the hydrogen and oxygen may be regarded as proceeding in two slightly different ways:

1. The concentration of the oxygen in the residual mother liquid, arising from the separation of comparatively pure crystals of copper, might force the reaction  $2\text{H}_2 + \text{O}_2 \rightleftharpoons \text{H}_2\text{O}$  from left to right.

2. This might be delayed until the solidification of the copper, plus  $\text{Cu}_2\text{O}$  eutectic begins to solidify and hydrogen then reacts with solid  $\text{Cu}_2\text{O}$ .

#### INFLUENCE OF MASS ON RATE OF COOLING

While it is well known that the mass or size of a casting has a distinct influence upon the character and position of the blowholes which may be formed in an ingot, and it is recognized that this is largely due to its effect upon the rate of cooling, it is not always understood how this operates.

Without wishing to be too dogmatic, I should like to indicate what appear to be the two most noteworthy factors in this connection, viz:

1. The slower the rate of cooling, the greater are the opportunities for the gases which can be liberated during solidification to escape from the liquid, and the more complete will be the chemical reactions which result in the formation of a compound gas which may also be insoluble. The time factor cannot be ignored in either of these two instances. Even when the variations of time are not sufficient to materially affect the total amount of gas that is liberated or formed, they might disturb the stage at which gas liberation, etc., occurs, and thus alter the position in which the blowholes are located in the ingot.

2. Anything that tends to restrict the free liberation of a gas while a metal is solidifying causes an increased internal pressure, and this increases the solubility of the gas. The effect in this direction is proportional to the square root of the pressure.

This has been demonstrated on a small scale in connection with aluminum by Archbutt<sup>8</sup> and others, who have found that sound castings free from pinholes can be produced by casting the metal in chill molds; while the same metal, cast in sand, would show pinholes to a marked degree.

Prytherch<sup>9</sup> has found the same kind of results by varying the mass of metal when dealing with copper containing hydrogen.

### REMOVAL OF GAS BY PHYSICAL MEANS

It follows, from what has already been said concerning the influence of pressure, that any means by which the partial pressure of a gas contained in the furnace atmosphere or otherwise in contact with the surface of a metal can be reduced will diminish the amount of that gas that can be dissolved in the metal. Accordingly, it was suggested by Rosenhain<sup>10</sup> and found by Archbutt<sup>8</sup>, that the passage of an inert gas, insoluble and chemically inactive through molten aluminum, results in the removal of the dissolved gases from the metal, with the result that when cast the ingots exhibit an extraordinary degree of soundness.

The principles underlying this suggestion have been found to be equally effective for copper and other metals and alloys.

### STEEL INGOTS

I now want to turn to a consideration of what appears to be one of the most fascinating aspects of the study of the influence of gases in the production of blowholes in castings.

This is to be found in that class of steel which has become generally known as "rimming steel." The feature of special importance in this connection lies in the fact that manufacturers intentionally aim at producing blowholes in the ingot; and, further, to control the stage at which they are formed in such a way as to obtain an ingot that possesses a good thick skin or jacket which, for all practical purposes, is entirely free from blowholes. Without going into a detailed description of the general characteristics or advantages of steel ingots of this kind, it may be useful to make the following observations:

1. An ingot of this kind will possess a thin skin of crystals which will have about the same chemical composition as the original liquid that entered the mold; this simply because a thin wall of solid is formed immediately the liquid comes into contact with the mold.

2. Beneath this outer surface there is:

- (a) A zone corresponding with the solid jacket which is free from blowholes. This portion not only contains less carbon than the average composition of the ingot, but is also much purer as regards sulfur and phosphorus, etc. Very thin pencil-like blowholes are often to be found

in this otherwise solid wall, more especially in the lower portions of the ingot.

(b) Immediately below the solid rim or wall (i.e., nearer the center of the ingot), blowholes are to be found which are somewhat semiglobular in type. These are often described as "intermediate" blowholes, to indicate that usually they are located midway between the side walls and central axes. At this zone, there is a concentration of impurities in the steel.

(c) The center portion is less pure than the average composition of the steel; and, as a rule, contains globular blowholes irregularly distributed throughout this part of the ingot.

(d) Ingots of this type contain little or no true pipe, but merely a number of blowholes lying just below the top crust of the ingot.

A large number of investigators have contributed to the study of this interesting problem; and, in recent years, a considerable amount of useful and important data relating to it have been published. Many views and tentative suggestions have been put forward, in an attempt to explain the principles which govern the position in which blowholes may be formed in steel ingots in general; and, for the most part, the ultimate object has been to obtain a better working hypothesis with regard to "rimming" ingots in particular.

It is not here being suggested that manufacturers find much serious difficulty in the production of this type of steel; but, I feel we have not got a perfectly satisfactory mental picture of the changes that have taken place during its solidification.

In conjunction with H. N. Jones<sup>11</sup> I undertook to study certain aspects of this problem for the Heterogeneity Committee of the British Iron and Steel Institute some time ago, and the work is still being extended.

The object of these experiments was to examine the influence of varying amounts of oxygen and carbon upon the internal character of the ingots, with special reference to the positions and general distribution of the blowholes in the ingots. Every effort was made to standardize the method of procedure, and eliminate, as far as practicable, all variables other than those under consideration. Quite briefly the procedure was as follows:

Sixteen pounds of commercial iron in the form of Armco iron rods was melted in a high-frequency furnace. After a specified temperature had been reached, a definite amount of oxide of iron, corresponding to 0.195 per cent of oxygen, was added to each experimental melt and sufficient time allowed for this oxide to dissolve in the metal. The slag was then removed from the surface of the metal, the necessary carbon in the form of a synthetic iron-carbon alloy was added, and then different quantities of metallic aluminum introduced to each melt belonging to a given series, and the metal cast at a constant temperature.



By proceeding in this manner, it was assumed that the amount of oxygen present, for any given series of constant carbon, was the same immediately prior to the introduction of the aluminum; and, that the oxygen left in the metal, just before casting, was inversely proportional to the amount of aluminum used.

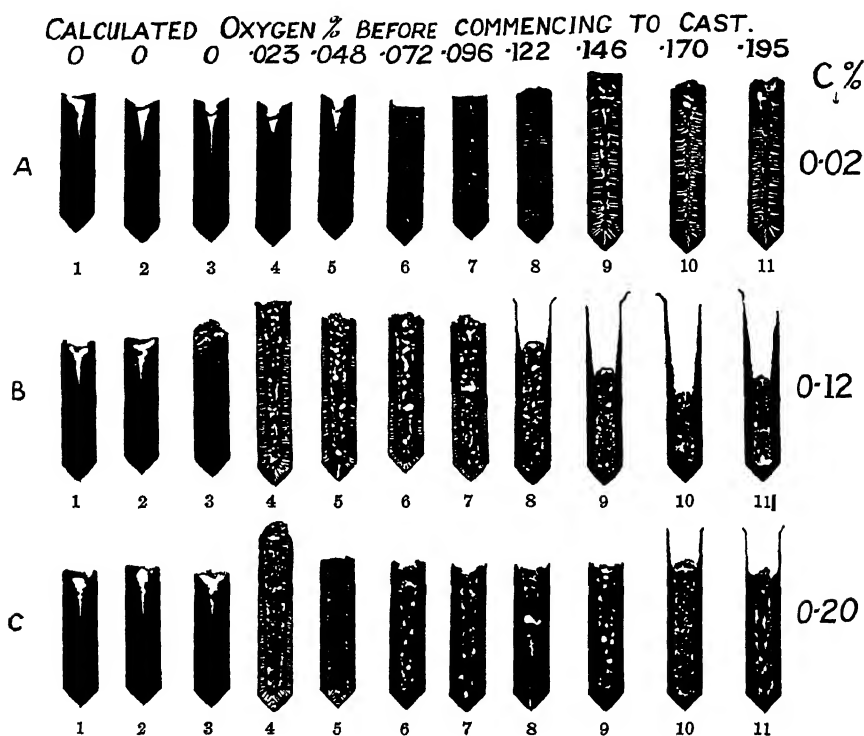


FIG. 3.—INGOTS CONTAINING VARYING AMOUNTS OF OXYGEN FOR CONSTANT CARBON.

On passing from one series to another (Fig. 3) containing a higher percentage of carbon, however, the residual oxygen present would tend to be further decreased, owing to the reducing action of the increased carbon present.

Needless to say, the intensity of this action would be greater as the amount of oxygen left in the metal after the addition of aluminum increased.

Before discussing the various details of the different types of ingots that have been obtained by proceeding in the manner just described, there are a few observations which should be clearly emphasized, if confusion is to be avoided.

In the first place, I think it can be claimed that practically every type of ingot known in the steel industry is represented in these series of experimental casts. Further, they clearly illustrate the influence of

varying percentages of oxygen and carbon upon the internal characteristics of ingots produced under commercial conditions. Nevertheless, it should be recognized that considerable care and thought must be exercised in endeavoring to translate the results into terms of everyday steelmaking practice.

### EFFECTS OF MASS

It is necessary to draw special attention to the effect of mass, or the small size of the ingots under consideration. Obviously, this means that the ingots have solidified at a very rapid rate, even when compared with what would be commercially regarded as a small ingot of, say, half a ton.

Broadly speaking, the effect of a decrease in size, resulting in greater rapidity of cooling, is to diminish the time during which chemical reactions giving rise to the formation of gas can take place; and, likewise, to decrease the ease with which gases so generated escape from the ingot during its solidification. This means that the character or type of the ingot obtained for any given oxygen and carbon content will tend to change, by decreasing the size of the ingot in such a manner as to give an effect similar to that a lower oxygen content would have, without decreasing the size of the ingot.

Conversely, for example, if we take ingots No. 7, for each of the series illustrated, an increase in the size of ingot would have an effect that would correspond to a type having a higher oxygen content than No. 7, for a particular series.

### OXYGEN CONTENT

It is desirable to again state that the ingots under discussion were synthetically made; and that the oxygen percentages have not been determined by analyses.

With regard to series A, I think the discrepancy in this connection would be found to be small, or to be more precise, I believe the differences between the oxygen contents of series A on going upwards from ingot No. 3 to No. 4, and so on, will be found to be close to 0.024 per cent.

This will apply, to a lesser extent, on passing from one series to another containing a higher percentage of carbon; and the variations in this respect will, no doubt, become more intensified for a given series, as the oxygen content of that series becomes greater.

The reason for this statement is that the carbon was introduced to the melt after aluminum was added; and, therefore, the tendency for the reaction  $\text{FeO} + \text{C} \rightleftharpoons \text{Fe} + \text{CO}$  to proceed from left to right would increase both as the amount of oxygen left in the metal prior to the addition of carbon was greater and also as the amount of carbon added was higher.

That these general observations are correct, can be gathered from a study of the character of the ingots themselves. In spite of these vari-

ables, I would like to emphasize that they in no way mitigate against the qualitative value of the results, as indicating the influence of progressively increasing amounts of oxygen upon the character of the ingots produced.

There is one further point which should be mentioned; viz., that, with the conditions under which these experiments were made, the metal does not appear to have taken up much, if any, more oxygen than was intentionally added. In other words, the much higher saturation limits for the solubility of oxygen in iron for high temperatures, which have been found by Herty<sup>12</sup>, do not seem to have been reached.

Before discussing the various types of ingots and their bearing upon the question of "rimming," a few observations relating to conclusions of previous workers may be useful.

Thus, for example, with regard to the question of the solubility of CO and CO<sub>2</sub> in steel, concerning which there has been considerable uncertainty, it may be said that the supposed solubility of these two gases has been based on the fact that they are found in the gases collected during solidification, or extracted from solid steel. As a result of investigations in this field, Klinger<sup>13</sup> has arrived at the following conclusions, viz:

1. The CO and CO<sub>2</sub> found according to the extraction method are purely reaction gases which originate during the estimation.

2. The chemical decomposition methods of Goutal and Vita cannot be considered for a gas estimation, as the first yields only reaction gas; and the second, owing to the means of solution adopted, provides no satisfactory results.

3. On the basis of the solubility experiments carried out with CO and CO<sub>2</sub> on iron, the solubility of these gases in steel must be denied.

Herty, in discussing the paper by Kinzel and Egan, on the equilibrium of the system iron oxide-carbon in molten iron, says:

The important application of Dr. Kinzel's work is that it apparently shows the solubility of CO is very low in steel. . . . Until recently, I had considered that the "rimming" action in "rimmed" steels was due to one or both of two possibilities:

- (1) CO eliminated on solidification owing to drop in the solubility of CO in the metal when it passes from the liquid to the solid state, and (2) CO developed in the reaction between carbon and FeO. . . . particularly at the solidifying surface. . . . Therefore, the explanation for rimming of steel in a mold, which of course applies equally well to a small test mold, is this: A solid surface is required to bring about the carbon-iron oxide reaction.

After much careful consideration of this complicated problem, I have come to the conclusion that Herty's view is practically correct.

It would, however, be very useful if we could extend it somewhat, and obtain a more precise idea of the part the solid surface takes in the changes that occur. In this connection, there can be no doubt that the reactions take place within the liquid layer immediately adjacent to

the solid surface; but, the latter is merely incidental and does not, itself, as a solid surface, play any direct role in the reactions. In other words, it is in no sense acting as a catalyst. Its function is that it is a surface from which heat is being rapidly conducted away by means of the solid shell, etc., and, thus, a marked temperature gradient between the solid surface and liquid is maintained. It is this chilling or sudden cooling action that intensifies the reactions that are associated with the "rimming" phenomena. This must tend to diminish as the thickness of the solid crust increases and practically terminates when dendritic crystallization ends. As will be seen later, however, coincident with the diminution of the chilling, or supercooling, influences, more time is permitted for the reactions to proceed, and these two factors tend to balance each other during the process of rimming.

I am of the opinion that the primary cause of the reactions being forced to take place in the liquid near the crystallizing surface is the preferential segregation of the oxygen and carbon in the liquid immediately facing the solid crystals of purer metal, which are being deposited on the walls of the ingot. Needless to say, the extent or degree of this preferential segregation, intensified by a marked temperature gradient, must be more pronounced than would be anticipated from a consideration of conditions of equilibria brought about by slow rates of cooling. Indeed, it is possible that rapid cooling of the liquid might cause precipitation of an oxygen-rich phase in the liquid, prior to the formation of any solid. In my opinion, it appears to be essential to consider that the reaction that gives rise to the formation of CO during rimming must take place in the liquid itself. There is real difficulty in visualizing how such gases could avoid becoming entrapped within the crystal dendrites, and the bubbles subsequently growing by crystallization proceeding around them, if the gas were, in fact, being formed at the interfaces of the solid and liquid. I found much the same difficulty when it was thought that the effervescing action was due to the liberation of CO, resulting from a marked decrease in the solubility of that gas with a change from the liquid to the solid state.

We can, I think, most satisfactorily explain the effects of varying amounts of oxygen and carbon in liquid iron and steel upon the internal character of the ingots produced, along the following lines.

Carbon and oxygen can co-exist in a state of equilibrium in molten iron, in much the same way that hydrogen and oxygen can exist in the molten copper, without giving rise to the liberation of CO, on the one hand, or H<sub>2</sub>O, on the other.

For the iron-oxygen carbon, this can most conveniently be expressed by the following reversible reaction:  $\text{FeO} + \text{C} \rightleftharpoons \text{Fe} + \text{CO}$ . This, of course, necessitates the assumption, based on purely theoretical considerations, that there is a limited solubility of CO in liquid iron. The

extent of this theoretical solubility need only be small; indeed, so small as to be completely neglected from the point of view of the practical aspects of rimming steel during solidification. As in all balance reactions of this kind, an increase in either of the components on the left-hand side will tend to force the reactions to proceed from left to right. When, however, the concentration of carbon is very low, say, something of the order of 0.02 per cent, the oxygen can be increased to above 0.2 per cent for temperatures up to 1650° C. without giving rise to the liberation of CO. That is to say, these quantities of dissolved carbon and FeO are incapable of increasing the amount of CO beyond the very limited extent to which that gas can be dissolved in the liquid metal as cooling proceeds down to that at which solidification commences. Nevertheless, it will be observed that, in the A series of ingots, where the carbon content was only 0.02 per cent, there are distinct indications of blowholes, more especially in those instances in which the quantity of oxygen was high. The explanation of this cannot be found, on the basis that there has been a greater natural tendency for the  $\text{FeO} + \text{C} \rightleftharpoons \text{Fe} + \text{CO}$  to move from left to right, while the temperature was falling down to that at which freezing begins. Indeed, from theoretical considerations, the reactions must tend to proceed in the opposite direction.

In steelmaking, it is known that rising temperatures cause the reaction to go in a positive direction; and Herty's<sup>14</sup> experimental data relating to the solubility of oxygen and carbon at different temperatures proves this.

When solidification starts, however, segregation of both carbon and oxygen occurs, which means that there will be a concentration of both these elements in the residual liquid near the freezing surface; and, in consequence, the reaction between oxygen and carbon must commence with the formation of CO. This, of course, must give rise to the liberation of CO, within the liquid adjacent to the crust or solid wall of metal.

When the percentage of carbon present is low, as in series A, this additional CO is generated and liberated in small amounts at a comparatively late stage; and when the mass, as a whole, is in a pasty stage. In other words, at a time and under conditions that cause it to be almost entirely entrapped in the ingot, with the formation of blowholes throughout the ingot causing a swelling or raising of the upper surfaces of the ingot during solidification.

In some respects, the position is much the same as regards the period at which the gas is generated, even when the carbon content is higher, say up to about 0.20 per cent, providing the oxygen content is low. This can be seen in ingots No. 4, series A, B and C. These ingots are typical examples of what occurs with the formation of small quantities of gas during the solidification period. When, however, the carbon content of the metal is higher than what may be described as the critical minimum

of about 0.02 per cent, and the oxygen content is raised above, say, ingot No. 4 for series C, the stage of solidification at which the segregating oxygen and carbon in the liquid layer near the solid crust becomes sufficiently concentrated to cause the reaction  $\text{FeO} + \text{C} \rightleftharpoons \text{Fe} + \text{CO}$  to move to the right, occurs relatively earlier. There is a more generous liberation of gas, but an increased opportunity for it to escape through the liquid interior.

Another point to remember, in this connection, is that as the carbon increases there is an increased opportunity for the gas generated during solidification to escape, because the higher carbon widens the range over which solidification takes place. While this is not large for small increments of carbon, I feel it is a factor of some importance and should not be entirely overlooked. Hence, though much more gas is generated in this and other series, with increasing oxygen, than with series A, far less of it becomes entangled or entrapped in the form of blowholes within the solid metal.

In passing, it might be mentioned that in the rimming of a commercial ingot there is a degree of activity of the above-mentioned reactions at which the stream of liberated gas rising through the liquid near the solid crust causes the well-known "effervescing" phenomenon. This, however, is not so marked as to cause the liquid as a whole to boil in the mold, and rising in the mold during solidification does not occur because the gas is freely escaping through a perfectly liquid medium. The sweeping action caused by the rapidity of this rising stream of small gas bubbles effectively prevents any of them from attaching themselves to the solid crystals of the crust, or shell. Incidentally, it should be noted that this bubbling action causes a steady circulation of the liquid interior; this mixes the segregating impurities in with the main body of the liquid. The stirring action also prevents a marked temperature gradient being set up between the liquid near the solid crust and that of the interior of the liquid; but, at the same time, it maintains marked temperature gradient between the solid wall and liquid interior. In this manner, the intensity of the chilling or supercooling effects of the wall are maintained, as well as the character of the freezing during the whole period of rimming.

It is interesting to note that, with these small ingots and with series C containing 0.12 per cent of carbon, there is a decidedly increased tendency to produce a solid rim, without rising or boiling in the mold, on passing from No. 5 to No. 7. Even in No. 7, however, the lower part of the ingot shows the blowholes lying quite near to the skin, very much like those that are frequently found in an ingot from a rimming charge.

I feel confident that liquid metal of the composition such as was cast into ingot No. 5 would show all the characteristics of rimming if it were cast in the form of large ingots, this simply because the slower rate of cooling would give an increased opportunity for the gas to be formed and

freely liberated during freezing. While ingot No. 7, if cast in a larger mass, would almost certainly display a tendency to boil like, say, Nos. 8, 9, etc., of the same series.

With this series of small ingots, it is significant to note that it is only when the metal contains so much oxygen as to cause it to boil in the mold, or even in the crucible prior to casting, that a perfectly solid rim is obtained. Under these conditions, the metal is so active that the well-known "box-hat" type of ingot is obtained.

The importance of this observation rather definitely implies that, when such small ingots are being cast, the necessary free liberation of gas corresponding with the needs of rimming is obtained only when so much oxygen is present as to cause vigorous boiling. Under otherwise identical conditions, but with higher carbon, say 0.20 per cent, the rimming characteristics are revealed with considerably lower oxygen percentages. With ingots of the size under consideration, this is largely due to the wider range of freezing temperature of the higher carbon mixture and the effect of the carbon upon the reactions; viz.,  $\text{FeC} + \text{C} \rightleftharpoons \text{Fe} + \text{CO}$ .

On this conception of the process of rimming it would be expected that there should be a close relationship between the loss of carbon and oxygen from the steel during freezing, and this should be reflected in the composition of the rimming portion of the ingot.

Rather clear indications of this are revealed in a set of figures given by H. L. Geiger<sup>15</sup> in his discussion on a recent paper by W. R. Fleming. Referring to an ingot, "which was poured at a medium temperature, and a composition of carbon 0.07 per cent, and manganese 0.37 per cent by analysis," he said, "this heat had an FeO content of 0.220 (0.048 per cent oxygen) in the bath. Average analyses of the case made for oxygen of these heats show 0.015 to 0.020 per cent, while the core shows the presence of about 0.04 to 0.05 per cent oxygen. Analysis of the case for carbon reveals 0.04 to 0.05 per cent, while the core will reveal about 0.07 per cent:

"CARBON IN HEAT	CARBON IN RIMMING	LOSS OF CAR- BON DURING RIMMING	OXYGEN IN HEAT	OXYGEN IN RIMMING	LOSS OF OXY- GEN DURING RIMMING
0.07 per cent	0.04-0.05 per cent	0.025 per cent	0.048 per cent	0.015 to 0.02 per cent	0.0305 per cent"

It is interesting to note that the decrease in the carbon and oxygen in the rimmed portion of the ingot, as compared with that present in the original liquid, closely corresponds to that required for carbon monoxide.

If additional evidence can be obtained confirming an approximation to this ratio, it will strongly support the view that rimming is caused by chilling or supercooling effects disturbing the conditions of equilibria and causing abnormal segregation, thus forcing the reaction of oxide of iron and carbon to take place.

These differences are not revealed in the composition of the core of the ingot, where the chilling influences have been reduced to a minimum. In other words, though the core contains a similar amount of oxygen and carbon as the original liquid, the rimming action ceases when the cooling rate becomes relatively slow.

There is yet another angle from which the subject may be examined. There seem to be good reasons for supposing that the well-known vigorous boiling action, which can be observed when testing for "heat" by means of trying a rod in a bath of steel prior to tapping, is brought about by changes which in all probability are similar to those that occur during the rimming of an ingot. This has already been mentioned in the discussion by Geiger<sup>15</sup>.

This boiling is caused, undoubtedly, by the formation and liberation of CO, but it is not obvious how this is brought about, and it has been the subject of much speculation.

As previously mentioned, from purely theoretical considerations, the liquid metal  $+FeO + C \leftarrow Fe + CO$  reaction should be in the direction indicated for falling temperatures; and in the reverse direction with rising temperature. This is supported by the fact that a rising temperature during steel refining accelerates the boil, and vice versa.

Then, again, the essential features have been further experimentally verified by Herty, who has found that the degree of solubility of FeO (oxygen) and carbon increases with falling temperature.

In face of these considerations and facts, it must be evident that, with normal slow cooling under conditions which would not cause a drastic disturbance of equilibrium, liberation of CO could not occur.

With the sudden local cooling, however, such as occurs during "rodding," etc., we know that vigorous liberation of CO takes place. We are, therefore, compelled to conclude that, under these conditions, a new constituent or phase is at least momentarily brought into existence, which causes the carbon to react with the oxygen in the bath, and the gaseous product of this reaction escapes before it can be re-absorbed by the metal through which it passes.

In the first place, we might be inclined to take the simple view; namely, that the new phase consisted of solid metal, and that the FeO liberated in consequence of this change reacts with the carbon in the liquid. If, by this, we were to consider that the amount of FeO thus separating or segregating would correspond to that which would normally separate with slow crystallization, the explanation could scarcely be regarded as adequate.

The amount of solid that could be formed during "rodding" must be infinitesimal, as compared with that contained in a steel-furnace charge; and, therefore, if the amount of FeO segregating was in accord with slow crystallization the artificial boil could not cause a degree of



reactivity which would cause a material drop in the carbon content of the bath.

It is, however, conceivable that the sudden cooling might cause the momentary precipitation of a new liquid phase, in the form of a cloud of globules containing a high concentration of FeO. This might occur either with or without the formation of particles of solid metal. Under these conditions, a relatively violent reaction would take place that would account for the known facts.

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## Studies upon the Widmanstätten Structure, VII—The Copper-silver System

BY CHARLES S. BARRETT,\* MEMBER A.I.M.E., HERMANN F. KAISER† AND ROBERT F. MEHL,‡ MEMBER A.I.M.E.

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THE copper-silver system presents several points of special interest in the study of segregate structures. The system is simple eutectic, with limited solid solutions terminal with the pure component metals. The extent of solid solubility decreases with decreasing temperature for both the copper-rich and the silver-rich alloys, thus offering a possibility for the formation of Widmanstätten figures and also a possibility for aging after quenching. In contrast to the structures studied previously the structures in this system are unique in their origin, for one terminal solid solution will precipitate the other, and vice versa. In most of the other systems for which crystallographic data on the precipitation (or transformation) process are available, either intermetallic compounds or intermediate phases partake in the decomposition process; the absence of such phases thus distinguishes this system. The lattice structures of the two solid solutions are identical in type, differing in lattice spacing by approximately 10 per cent; because of this it seems difficult if not impossible to predict on the basis of present theory either the outward form of the precipitate or the lattice orientation relationships between matrix and precipitate.

The eutectic temperature in the copper-silver system<sup>1</sup> is 779° C. At this temperature copper dissolves 4.3 atomic per cent (7.0 weight per cent) of silver in solid solution; this solid solubility decreases to zero at room temperature.<sup>2</sup> Silver at the eutectic temperature retains 14.0

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\* Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

† Division of Physical Metallurgy, Naval Research Laboratory, "Bellevue," Anacostia, D.C.

‡ Director, Metals Research Laboratory, and Professor of Metallurgy, Carnegie Institute of Technology.

<sup>1</sup> See recent paper by D. Stockdale [The Solid Solutions of the Copper-silver System. *Jnl. Inst. Metals* (1931) 45, 127] and the extended discussion thereto, where most previous work is quoted. No attempt will be made here to review data on the constitution of this system; the data on solid solubilities particularly are not all in agreement.

<sup>2</sup> N. Ageew, M. Hansen and G. Sachs: Entmischung und Eigenschaftsänderung übersättigter Silber-Kupferlegierungen. *Ztsch. Physik* (1930) 66, 350; see Stockdale, *op. cit.*

atomic per cent (9.0 weight per cent) of copper in solid solution, but only approximately 0.2 atomic per cent (0.1 weight per cent) copper at room temperature.<sup>3</sup> The age-hardening characteristics of the alloys have been studied by a number of investigators.<sup>4</sup>

### CRYSTALLOGRAPHY OF PHASES

Both copper and silver are face-centered cubic;  $a_0$ , the side of the unit cell,<sup>5</sup> for copper is 3.608 Å. and for silver is 4.078 Å. At the maximum solid solubility in copper-rich alloys (4.3 atomic or 7 weight per cent silver)  $a_0$  is 3.633 Å.; at the solubility limit at room temperature the cell dimensions are indistinguishable from those of pure copper.<sup>6</sup> At the maximum solid solubility in silver-rich alloys (14 atomic or 9 weight per cent copper)  $a_0$  is 4.025 Å.; at the solubility limit at room temperature the unit cell is practically identical with that of pure silver. The values of  $a_0$  in either solid solution vary approximately linearly with composition by weight.

### THE PRECIPITATION PROCESS

Ageew, Hansen and Sachs<sup>7</sup> have shown that precipitation in both copper-rich and silver-rich alloys is accompanied by a series of anomalies. From work on other systems it would be expected that the lattice dimensions of either solid solution matrix would change gradually with rejection of the solute element corresponding to a gradually diminishing concentration of solute in the matrix. Such, however, is not the case. It was observed that the X-ray diffraction lines from the matrix or parent solid solution appear unchanged in position on a photogram of a partially precipitated alloy, and that a new set of lines appears, corresponding to the lattice of the completely decomposed solid solution. No trace of diffraction lines of the precipitate was found, owing to the small amounts of precipitate formed. The intensity of the old set of lines decreases with increasing precipitation while the intensity of the new set increases. It is concluded from these data that the precipitation process consists in an immediate and complete rejection of solute in discrete transformed regions, rather than a gradual rejection of solute throughout the alloy. Furthermore it was found that the hardness values during aging were not

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<sup>3</sup> N. Ageew and G. Sachs: Röntgenographische Bestimmung der Löslichkeit von Kupfer in Silber. *Ztsch. Physik* (1930) **63**, 293; see Stockdale, *op. cit.*

<sup>4</sup> See, for example, Ageew, Hansen and Sachs, reference of footnote 2. Many papers have been published on this subject.

<sup>5</sup> M. C. Neuburger: Gitterkonstanten 1933. *Ztsch. Krist.* (1933) **86A**, 395.

<sup>6</sup> N. Ageew and G. Sachs: Reference of footnote 3.

<sup>7</sup> N. Ageew, M. Hansen and G. Sachs: Reference of footnote 2.

proportional to the quantities of the precipitated phase (as measured by the relative intensities of the old and new set of diffraction lines), at least at high solute concentrations and low aging temperatures, and that the changes in electrical conductivity were also anomalous. These statements apply to both copper-rich and silver-rich alloys.

The new set of diffraction lines was found to be diffuse, which was interpreted as evidence for either internal strains or extreme fragmentation of the matrix during precipitation. It was observed that the new lattice was largely of random orientation with respect to the old.

Wiest<sup>8</sup> in a later paper discovered further anomalies by studying the aging of single crystals of an alloy with 5 weight per cent silver. Three separate hardness maxima were demonstrated on the aging curves, which suggested to Wiest that three separate hardening processes obtained during the aging of these alloys, only the last of which could be directly ascribed to real precipitation. The first maximum occurs before appreciable change in lattice dimensions, and the second at the beginning of change in lattice dimensions. It seems possible that at least one of the first two hardening processes consists in the generation of internal strains, possibly the second (Ageew, Hansen and Sachs' diffuse lines would lend support to this), and one is inclined to ascribe the first in the usual way to a pre-precipitation aggregation of solute atoms ("knots"), but there is nothing really definite known, except that several processes are operative and that the nature of these processes and their interrelations are indeed complicated. The complications inherent in this system are also evident in the results of the present work.

## OUTWARD FORM OF PRECIPITATE

### *Heat-treatment*

Published photomicrographs of copper-silver alloys show no structures that may be definitely identified as Widmanstätten figures. Slow cooling usually causes the precipitate from the solid solution in silver-rich alloys to be arranged in a structure resembling pearlite.<sup>9</sup> Occasionally structures are obtained showing "needles" similarly oriented in a rough way.<sup>10</sup> Quenching and reheating have been shown to develop a structure

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<sup>8</sup> P. Wiest: Aushärtungsvorgänge bei Silber-Kupfer-Einkristallen. *Ztsch. f. Metallkunde* (1933) **25**, 238.

<sup>9</sup> See, for example, M. Hansen: Die Löslichkeit von Kupfer in Silber. *Ztsch. f. Metallkunde* (1929) **21**, 181; M. Hansen: Die Härte silberreiche Kupfer-silberlegierungen. *Ztsch. anorg. Chem.* (1930) **186**, 41; A. L. Norbury: The Effect of Quenching and Tempering on the Mechanical Properties of Standard Silver. *Jnl. Inst. Metals* (1928) **34**, 145.

<sup>10</sup> M. Hansen: Two references of footnote 9.

somewhat like martensite or troostomartensite in appearance distributed in patches, but lacking the precise geometrical arrangement that characterizes martensite.<sup>11</sup>

In copper-rich alloys "needles" suggesting a regular arrangement of precipitating plates, but not sufficiently well developed to prove this, have been observed.<sup>12</sup> This structure is also somewhat reminiscent of pearlite.

*Copper-rich Alloys.*—Two alloys were prepared using as starting

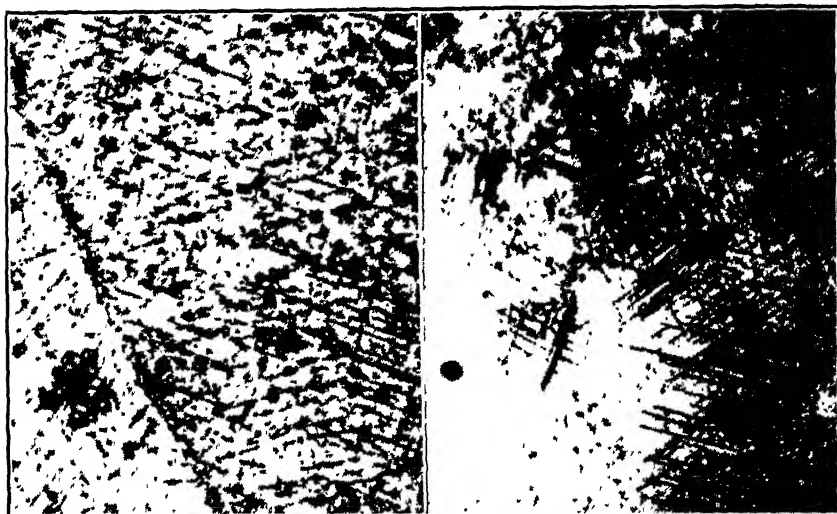


FIG. 1.—3 PER CENT SILVER ALLOY. SHOWING WIDMANSTÄTTEN STRUCTURE IN TWO GRAINS.  $\times 1000$ .

Homogenized, quenched, annealed  $2\frac{1}{2}$  hr. at  $400^{\circ}$  C. Etched in ammonium hydroxide plus hydrogen peroxide.

FIG. 2.—3 PER CENT SILVER ALLOY. SHOWING WIDMANSTÄTTEN STRUCTURE ON TWO SIDES OF A VERTICAL TWIN BOUNDARY.  $\times 1000$ .

Hammered, homogenized, cooled from  $750^{\circ}$  to  $408^{\circ}$  at  $7^{\circ}$  per hour, then cooled to room temperature in 5 minutes. Etched in ammonium hydroxide plus hydrogen peroxide.

materials Hilger "spectroscopically pure" copper and mint silver stated to be 99.9+ per cent silver. Portions weighed to approximate 7 and 3 weight per cent silver, respectively, and to give a total weight of approximately 50 grams, were melted in graphite in an evacuated tube held within an induction furnace;<sup>13</sup> the alloy was frozen in the crucible. The

<sup>11</sup> A. L. Norbury: Reference of footnote 9.

<sup>12</sup> Stockdale: Reference of footnote 1.

<sup>13</sup> No special analyses were made of either the stock metals or the final alloys, since variations in composition within a phase field are relatively unimportant in this work.

ingots were then annealed at  $705^{\circ}$  for 48 hr. for homogenization, and quenched. In view of Stockdale's experiments this treatment cannot be considered sufficient for homogenization; the ingots were found to contain free particles of eutectic silver. The difficulties in homogenization led to abandoning the 7 per cent alloy in favor of an alloy with less silver. The structures about to be described apply only to the 3 per cent alloy, to which, for this reason, the work was restricted. Annealing the quenched alloy at  $400^{\circ}$  for  $2\frac{1}{2}$  hr. developed the structure shown in Fig. 1, which evidently was a Widmanstätten figure of plates, but the structure



FIG. 3.—7 PER CENT SILVER ALLOY. SHOWING PEARLITE-LIKE STRUCTURE IN PATCHES WITHIN AN ORIGINAL GRAIN OUTLINED BY EUTECTIC.  $\times 500$ .

Hammered, homogenized, cooled  $7^{\circ}$  per hour from  $750^{\circ}$  to  $408^{\circ}$  C., then to room temperature in 5 minutes. Etched in chromic acid plus sulfuric acid.

was too fine for real resolution. The same alloy, held 2 hr. at  $800^{\circ}$  then furnace-cooled to  $400^{\circ}$  in  $2\frac{1}{2}$  hr. and finally cooled in vacuum to room temperature, produced a similar structure, though often only indistinct rounded particles of no obvious geometrical arrangement could be seen.

The development of a Widmanstätten structure in this alloy seemed to offer the same problems as that in silver-rich alloys, which were studied concurrently; it seemed likely in both cases that a very slow cooling through the initial stages of precipitation would be likely to develop the desired structure. For this purpose the alloy was first hammered, then annealed in graphite in partial vacuum at  $800^{\circ}$  for 19 hr., and subsequently cooled from  $750^{\circ}$  to  $408^{\circ}$  at a rate of  $7^{\circ}$  per hour in a

special "program-control" furnace, then normally to room temperature in about 5 min. This treatment gave a very well defined Widmanstätten figure, shown in Fig. 2.

*Silver-rich Alloys.*—These alloys were made from the same materials and in the same way as the copper-rich alloys. Alloys were prepared to contain 12, 9, 7, 4 and 3 weight per cent copper; they were annealed at  $765 \pm 10^\circ \text{C.}$  for 48 hr. This shorter time of annealing was found to be sufficient for homogenization.

These alloys were given a wide variety of heat treatments in an attempt to develop Widmanstätten figures. Great difficulty was encoun-



FIG. 4.—7 PER CENT COPPER ALLOY. SHOWING PLATE STRUCTURE OF PEARLITE-LIKE PRECIPITATE.  $\times 880$ .

Homogenized at  $765^\circ$  for 89 hr., furnace-cooled to  $350^\circ$  and held there for 22 hr. Then cooled in air. Etched with chromic-sulfuric acid.

FIG. 5.—4 PER CENT COPPER ALLOY. SHOWING CONCHOIDAL STRUCTURE, WHICH IS PROBABLY A STRAIN-ETCHING EFFECT.  $\times 200$ .

Homogenized at and quenched from  $765^\circ$ ; annealed 20 hr. at  $300^\circ$ . Etched with chromic plus sulfuric acid.

tered in this effort. Treatments consisting in fast or slow cooling from above the solvus curve to various temperatures below it, followed either by air cool or quench from these sub-solvus temperatures, gave structures that were like pearlite in appearance. Similar structures were obtained by quenching from super-solvus temperatures and reheating to various sub-solvus temperatures. These are illustrated in Figs. 3 and 4.

These pearlitelike structures were of no use in establishing a plane of precipitation. Close study of them showed the copper precipitate in the form of plates (Fig. 4), and though the surface intersections of these plates were seen occasionally to be quite straight, and to lie in nearly

parallel families, the curvature of the plates, and the lack of any precise alignment prevented any sort of crystallographic analysis. Structures of this sort were obtained with all alloys, with cooling rates as low as  $7^{\circ}$  per hour between  $750^{\circ}$  and  $408^{\circ}$  (7 and 4 per cent copper) and as high as a furnace cool. More rapid degrees of cooling failed to develop any recognizable structure, owing doubtless to the very slow diffusion that characterizes this system. Heat treatments consisting in a quench followed by a long anneal from  $200^{\circ}$  to  $350^{\circ}$  also formed the pearlite type of structure. Occasionally a quenching treatment followed by a prolonged heating at a sub-solvus temperature developed a structure which faintly

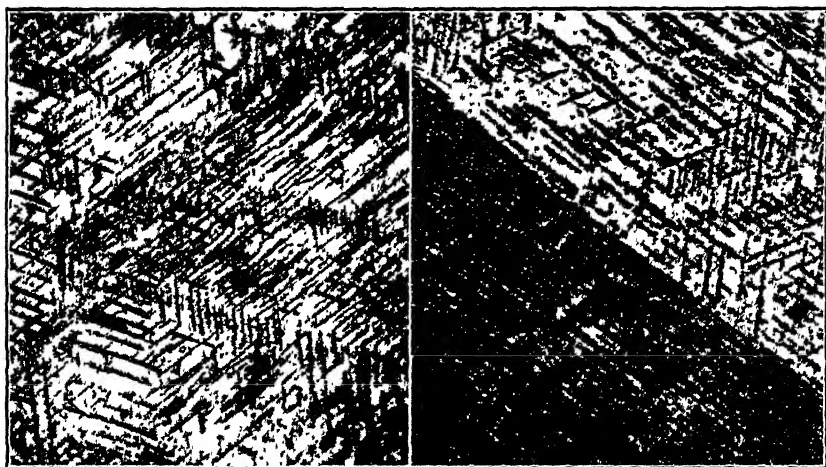


FIG. 6.—4 PER CENT COPPER ALLOY. SHOWING WELL DEVELOPED WIDMANSTÄTTEN FIGURE.  $\times 300$ .

Annealed at  $805^{\circ}$ , cooled in furnace to  $720^{\circ}$ , cooled between  $720^{\circ}$  and  $610^{\circ}$  at a rate of  $5^{\circ}$  per hour, then cooled to room temperature in 5 minutes. Etched with chromic plus sulfuric acid.

FIG. 7.—4 PER CENT COPPER ALLOY. SHOWING WELL DEFINED WIDMANSTÄTTEN FIGURE WITH TWIN BAND IN WHICH PRECIPITATE IS ONLY FAINTLY VISIBLE.  $\times 1000$ .

Same heat treatment as given in Fig. 6. Etched with chromic plus sulfuric acid.

resembles martensite, or more nearly the flow figures developed in overstrained bessemer steel by Fry's etching agent (Fig. 5). In fact, the figures observed are most probably etching effects resulting from strains accompanying the decomposition of the solid solution matrix.

At this point the closest approximation to a Widmanstätten structure was found in alloys cooled at extremely slow rates. For this reason even slower rates were applied, which ultimately produced Widmanstätten figures of a high degree of perfection. A 4 per cent copper alloy was annealed for 24 hr. at  $805^{\circ} \pm 5^{\circ}$  for homogenization, then cooled at a rate of  $5^{\circ}$  per hour between  $720^{\circ}$  and  $610^{\circ}$  in the "program control" furnace and then normally cooled to room temperature in 5 min. The type of structure obtained is shown in Fig. 6. It was observed that the



precipitated plates tended to arrange themselves as bands of parallel plates perhaps following lines of distortion from scratches suffered in earlier work on the specimen. This alloy proved satisfactory for analysis.

### *Plane of Precipitation*<sup>14</sup>

*Copper-rich alloys.*—A count was made of the number of directions taken by the traces of the silver-rich plates on the surface of polish of the 3 per cent silver alloy shown in Fig. 2. Of the 68 grains studied, all of which displayed a well defined structure, 38 were found to exhibit

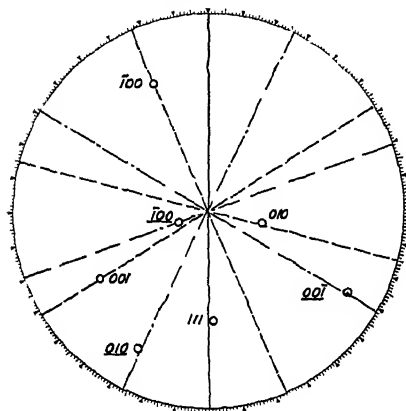


FIG. 8.

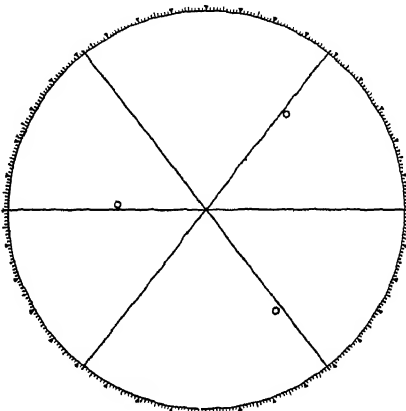


FIG. 9.

FIG. 8.—STEREOGRAPHIC PLOT OF PRECIPITATE TRACE DIRECTIONS AND TWIN DIRECTION FOR FIG. 2 (3 PER CENT SILVER ALLOY).

Plane of projection is surface of polish; solid line represents normal to trace of twin boundary; dashed lines represent normals to directions of precipitate traces in one crystal; dot-and-dash lines represent normals to direction of precipitate traces in crystal with twin relation; circles represent poles of planes accounting for traces; underlined indices represent indices of poles in crystal with twin relationship; other indices represent indices of poles in other crystal.

FIG. 9.—STEREOGRAPHIC PLOT OF PRECIPITATE TRACE DIRECTIONS.

For 3 per cent silver alloy, homogenized at 800° C., cooled in furnace to 400° C. in 2½ hr., and held at 300° for 5 hr. Plane of projection is plane of polish. Lines are normals to trace directions, small circles are {100} poles located by X-ray data.

three different directions of traces, and 30 showed two directions. No grain showed more than three directions. The directions in the grains exhibiting only two directions were always approximately 90° from one another. This evidence points strongly to a plane of the type {100} as the plane parallel to which the silver-rich plates lie.

An indirect method was next adopted to demonstrate the plane of precipitation. A grain was selected that showed a clearly marked twin

<sup>14</sup> As the study of the planes of precipitation and of the orientation of the precipitate in both terminal solid solutions proceeded, it became evident that the results would be very unusual. Because of this the findings were restudied several times. The results of these repeated studies are given here at a risk of seeming overcareful. This applies to the following section as well as to this section.

band (Fig. 2). A standard stereographic projection of a cubic crystal was prepared, showing not only the  $\{100\}$  and  $\{111\}$  poles, but also the same poles of a crystal formed from the first by twinning on a  $\{111\}$  plane. The assumption of a  $\{111\}$  twinning plane may confidently be made; both copper and silver are known to twin on this plane.

By rotation of this projection a position was found that would fully account for the directions of the traces on either side of the twin boundary, and also for the direction of the twin boundary, upon the assumption that the plates lay parallel to the  $\{100\}$  planes. This result is shown in Fig. 8; solutions of this sort on two different grains were obtained. This proof is not unique, for only an exhaustive search would prove the absence of alternative solutions.

In addition to these proofs, a specimen with large grains though with a less perfectly developed Widmanstätten figure was subjected to the usual sort of analysis, consisting in an X-ray determination of the orientation of the matrix lattice, and a matching of the trace normals with poles of the matrix planes. In each case  $\{100\}$  poles fell very close to the trace normals, as shown in Fig. 9.

These three separate analyses may be taken as proof that the silver-rich plates lay parallel to the  $\{100\}$  planes in the copper solid solution matrix.

*Silver-rich Alloys.*—A count of the directions taken by the copper-rich plates in the 4 per cent copper alloy, shown in Fig. 6, was inconclusive. Most of the grains showing good structures had three sets of traces at about  $60^\circ$ . No grains with four sets of traces were found, but later work indicated that the etching agent used was effective in revealing structure only on the matrix plane that displayed three sets of traces. This evidence points strongly to precipitation on  $\{111\}$  planes but does not entirely eliminate the possibility of precipitation on  $\{100\}$  planes.

An indirect analysis making use of the twinning plane was also used here. In every structure studied it was found that one set of precipitate traces lay accurately parallel to the twin boundary, which is the trace of a plane of the type  $\{111\}$ ; this in itself is proof that the plates lay parallel to a  $\{111\}$  plane in the solid solution matrix. The parallelism of plates and twin boundary may be seen in Fig. 7. This figure also

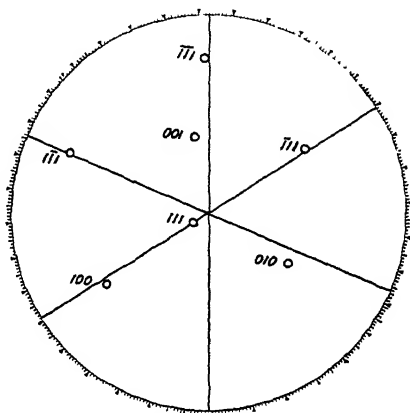


FIG. 10.—STEREOGRAPHIC PLOT OF ORIENTATION OF MATRIX AND OF DIRECTIONS OF PLATE TRACES IN 4 PER CENT COPPER ALLOY SHOWN IN FIG. 6.

Plane of projection is plane of polish. Circles and indices represent poles of matrix lattice as determined by X-rays. Lines represent normals to directions of plate traces.



also showed the precipitate reflections grouped near the matrix reflections of the same indices in such a way as to prove a coincident orientation of matrix and precipitate. This photogram is reproduced in Fig. 11. In the original photogram the  $\text{CuK}_\alpha$  and  $\text{CuK}_\beta$  reflections from both matrix and precipitate are visible; Fig. 11 shows only the stronger of the reflections from the precipitate, the  $\text{CuK}_\alpha$  line.<sup>18</sup>

The data from these photograms combined with data from a shifting film in the Weissenberg goniometer were sufficient for a stereographic plot of the orientation of matrix and precipitate lattices. Without exception the poles of each plane of the precipitate fell upon the poles of the planes of the matrix of the same index. Thus both lattices have the same orientation within a limit of error of one or two degrees.

It is interesting to note that this coincident orientation is the same as that observed for a layer of silver electrodeposited on a single crystal of copper.<sup>19</sup> The photograms of the latter structure are identical in type with those shown here.

*Silver-rich Alloys.*—No success was attained in determining the orientation of the precipitate in a sample showing a well defined Widmanstätten figure. Despite careful etching experiments designed to enrich the surface in the precipitate, no reflections from the precipitate lattice appeared on the photogram. The orientation of the precipitate was obtained, however, on an alloy that possessed the pearlite-like structure, and also on an alloy in which the precipitate took the form of rounded particles.<sup>20</sup> Both alloys contained 7 per cent copper. The first was cooled at a rate of  $7^\circ$  per hour from  $750^\circ$  to  $408^\circ$ , and then normally to room temperature; the second was cooled at a rate of  $7^\circ$  per hour from  $750^\circ$  to  $440^\circ$ , and then normally to room temperature. The intensity of the precipitate reflections was enhanced by preferential etching of the specimens.<sup>21</sup>

Reflections from the precipitate were found on five different oscillating crystal photograms. Their intensity was always low, but in all, 12 different reflections from the  $\text{K}_\alpha$  line were found that were strong enough

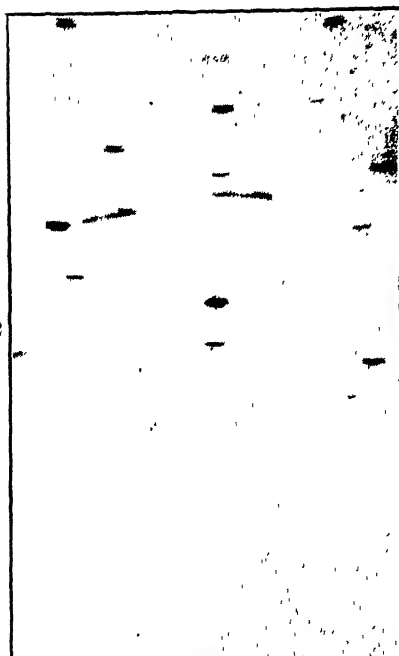
<sup>18</sup> Other spectra from the same X-ray tube proved the radiation to be purely that of copper (the presence of gallium in the target alone could have given an arrangement of spots similar to those observed and assigned to the precipitate). A faint Debye ring (from silver) through these spots, which did not have its counterpart in a ring through the matrix spots also proved the absence of spurious wave lengths.

<sup>19</sup> E. Schmid and G. Siebel: Über die Mischkristallbildung bei ein- und vielkristallinen Material. *Ztsch. Physik* (1933) 85, 36.

<sup>20</sup> Previous papers in this series have shown the orientation relationship between matrix and precipitate to obtain when the outward form of the precipitate possesses no obvious geometrical arrangement.

<sup>21</sup> The etchant used was equal parts of concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , which seemed to be much less effective for its purpose than the etchant used on the copper-rich alloys.

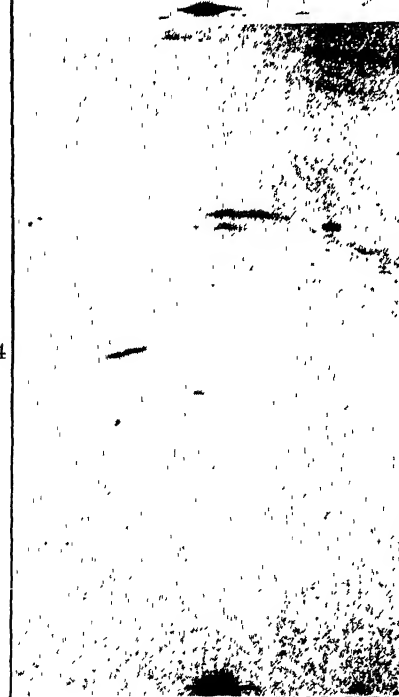
12



13



14



15



FIGS. 12-15.—CAPTIONS ON OPPOSITE PAGE.

to be identified. The best photogram contained six precipitate reflections. The reflections from the  $K_{\beta}$  line were too weak to be registered.<sup>22</sup>

The positions of these 12 reflections and of the corresponding reflections from the silver-rich matrix were the same as those observed for the copper-rich alloys. The relative intensities of the lines from the two phases were reversed, for those from the silver-rich phase now naturally showed the greater intensity. The precipitate reflections came from the  $\{111\}$ ,  $\{220\}$  and  $\{311\}$  planes; the rigor of the X-ray technique, and the correspondence between the reflection angles of these spots and the angles to be expected from the copper-rich phase, precluded their origin from spurious radiation. The reflections from the matrix were for the most part sharp, which proves the absence of matrix fragmentation and reorientation in these specimens.

### *Reorientation of Matrix*

During a study of the orientation of the matrix in partially precipitated silver-rich alloys, a phenomenon not hitherto described was observed. It had been pointed out by Ageew, Hansen and Sachs<sup>23</sup> that precipitation in these alloys is accompanied by a fragmentation of the matrix crystal, but these workers stated that the resultant crystals were largely if not entirely random in orientation. In the present work some matrix crystals were observed to fragment in such a way as to produce a small number of new orientations bearing a definite orientation relationship to the original matrix crystal.

A 4 per cent copper (silver-rich) alloy was annealed at 765° for 48 hr., quenched, and annealed in vacuo for various periods of time at 300°. As the annealing proceeded it was observed that the diffraction patterns obtained on a Davey-Wilson camera, consisting of sharp spots from the original matrix lattice, became progressively weaker, while a new set of diffuse spots, corresponding to those of the completely decomposed matrix (Ageew, Hansen and Sachs' "new lattice"), appeared and grew

FIG. 12.—PHOTOGRAM WITH OSCILLATING CRYSTAL AND STATIONARY FILM, SHOWING PARTIALLY REORIENTED MATRIX.

Intense sharp spots from original grain, weak streaks from reoriented matrix. 4 per cent copper alloy, homogenized and quenched from 765°, annealed 7 hr. at 300° C.  $MoK_{\alpha}$  and  $K_{\beta}$  X-rays.

FIG. 13.—PHOTOGRAM TAKEN UNDER SAME CONDITIONS AS FIG. 12 BUT WITH OSCILLATING FILM OF DAVEY-WILSON CAMERA.

Spots are from original grain, diagonal streaks from new orientations.

FIG. 14.—PHOTOGRAM WITH OSCILLATING CRYSTAL AND STATIONARY FILM, SHOWING COMPLETELY REORIENTED MATRIX.

4 per cent copper alloy homogenized and quenched from 765°, annealed 21½ hr. at 300° C.  $MoK_{\alpha}$  and  $K_{\beta}$  X-rays. A different grain than that of Figs. 12 and 13.

FIG. 15.—PHOTOGRAM TAKEN UNDER SAME CONDITIONS AS FIG. 14 BUT WITH OSCILLATING FILM OF DAVEY-WILSON CAMERA.

<sup>22</sup> The specimen used for this exposure was the second one described above. In all of these exposures unfiltered copper radiation was used; the exposure conditions were similar to those for the copper-rich alloys.

<sup>23</sup> Reference of footnote 2.

in strength, ultimately appearing alone on the photogram.<sup>24</sup> It required from 5 to 10 hr. of annealing to develop the new pattern from its faint beginning to its full intensity. The annealing time to bring about the first appearance of this pattern, however, varied in different grains from 7 hr. to a maximum of 38 hr. In all, nine different photograms were taken, which showed the presence of the diffuse pattern. Reproductions of some of these are given in Figs. 12, 13, 14 and 15. It is apparent that the diffuse pattern indicates a set of orientations quite different from the original orientation shown by the sharp spots. The relation between

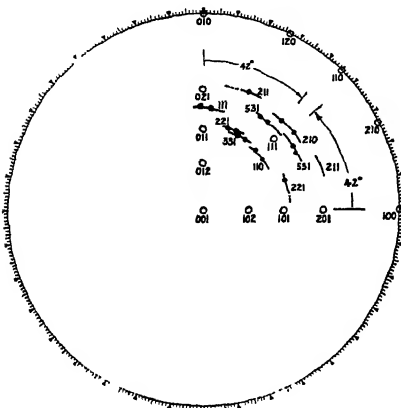


FIG. 16.

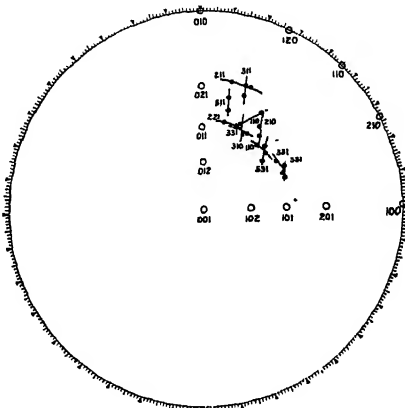


FIG. 17.

FIG. 16.—STEREOGRAPHIC PROJECTION OF REFLECTIONS IN FIGS. 12 AND 13.

Circles represent poles of original lattice, determined by intense, sharp reflections. Streaks represent new orientations causing weak diffuse streaks on photograms. Black dots indicate intensity maxima on streaks. Plane of projection is (001) of original matrix.

FIG. 17.—STEREOGRAPHIC PROJECTION OF REFLECTIONS IN FIGS. 13 AND 14.

Circles represent poles of original lattice, determined by photograms before reorientation had occurred. Streaks represent data from Figs. 13 and 14; black dots indicate intensity maxima on streaks. Plane of projection is (001) of the original matrix.

the old and the new orientations was determined by preparing a stereographic projection of the original matrix and superimposing the data from the diffuse pattern. The relationships thus found for two different grains are shown in Figs. 16 and 17, where the small circles represent poles of the original lattice and the streaks (with dots to indicate intensity maxima) represent the pole figure of the new orientations. For the case shown in Fig. 16, which represents a partially transformed grain, the new orientations may be derived from the original by a rotation of  $42^\circ$  in each direction about the [001] axis of the original lattice, with a deviation of  $\pm 5^\circ$  from this mean rotation. An identical relation was found for another grain during the early stages of the transformation, but when the diffuse pattern had reached full intensity the pole figure was as

<sup>24</sup> No diffraction spots from the precipitate were observed on these films.

shown in Fig. 17. The complex orientations of Fig. 17 may be derived from the original orientation by a rotation in each direction of  $42^\circ \pm 5^\circ$  about [100], [010] and [001] directions in the original matrix as axes.<sup>25</sup>

It might be suspected that these orientation relationships result from a simple twinning process initiated by the strains accompanying precipitation, but the indices of all twinning planes capable of developing these relationships are quite improbable. The average separation of the two intensity maxima on each streak was found to be  $6.6^\circ$ ; if this is used as a criterion for the choice of a suitable plane of symmetry serving as a twinning plane, the indices,  $\{hkl\}$ , for this plane would have to be such that  $h:k:l = 21:8:0$ . The usual twinning plane in the metals concerned here is the  $\{111\}$ . The indices for the plane of symmetry derived above are quite irrational for a twinning plane. Photomicrographs of the grains during the development of the new orientations show no twinlike formations, but rather a set of irregular lines resembling "suture lines"; some grains take on the appearance of that in Fig. 5.

It seems likely that the phenomenon can best be described as a recrystallization in which the recrystallized grains do not have random orientation but a restricted number of orientations bearing a relationship to the orientation of the grain from which they came. It will be remembered that cold-rolled metals bearing a preferred orientation will in some cases recrystallize to new preferred orientations.<sup>26</sup> The factors that determine the geometrical relationship between the new and the old preferred orientations are as yet unknown.

While the recrystallized grains cannot be individually recognized after a low-temperature anneal of several hours, because of their small size, further heating at higher temperatures may be expected to develop them to visible dimensions. The structure shown in Fig. 3 seems to support this. The specimen shown had been aged at room temperature for two years, then rehomogenized and slowly cooled. The original large grains, as outlined by particles of eutectic, now show a division into a number of smaller areas. The structure in this respect also is very much like that of pearlite.

The type of matrix fragmentation described above was not observed in all alloys bearing a segregate structure. The specimen with the well developed Widmanstätten figure shown in Fig. 6, for example, suffered no fragmentation, for the X-ray photogram yielded spots showing a single matrix orientation. Quenched alloys seemed more susceptible to fragmentation than slowly cooled alloys, which is consistent with the idea that strain induces this fragmentation.

<sup>25</sup> A preliminary note on the crystallographic features of the fragmentation was published by two of the present authors in *Physical Review* (1932) **40**, 1035.

<sup>26</sup> R. Glocker and H. Widmann: *Ztsch. Metallkunde* (1929) **18**, 41; R. Glocker: *Materialprüfung mit Röntgenstrahlen*, 332-342. Berlin, 1927. Julius Springer.



No similar fragmentation process could be found in copper-rich alloys. Several photograms taken from cold-drawn wires of the 6 per cent silver alloy before and after precipitation showed an unchanging matrix preferred orientation.

### POWDER DIFFRACTION SPECTRA

In an attempt to explain the unusual character of the results obtained a search was made for transition lattices. Photograms were prepared of quenched and annealed powders of the 4 per cent copper and the 3 per cent silver alloys, using a set of Phragmén cameras with copper radiation. The intensity of the diffraction lines from the original matrix was found to decrease gradually upon annealing, and that of the completely decomposed matrix to increase gradually. Except for the lines from these two lattices, no other lines were found, from which it may be concluded that transition lattices are not present in great amounts. The rate of decomposition of the matrix phase in the 4 per cent copper alloy was found to be similar to that observed by Ageew, Hansen and Sachs;<sup>27</sup> precipitation was observed to be three-quarters complete after annealing 15 min. at 300°. A much slower rate was found for the 3 per cent silver alloy; precipitation was about one-fifth complete after annealing 17 hr. at 300°. No appreciable broadening of diffraction lines was found for these powdered samples, though such broadening has been reported for aggregates by Ageew, Hansen and Sachs.

### DISCUSSION OF RESULTS

It has been observed in the work reported in this series of papers that a plate precipitated from a solid solution contains parallel to its surface a plane of atoms bearing a striking similarity in pattern and interatomic distances to the plane of atoms in the parent solid solution to which the plate lies parallel. It has been assumed that the plane of atoms in the precipitate forms directly from the plane of atoms in the parent solid solution by an adjustment in atom positions. The occurrence of such similar planes was taken as a condition necessary to the formation of a plate structure. The growth of such nuclei to gross plate structures was considered as resulting from normal growth, the atoms on parallel planes in the solid solution taking their positions in the precipitate lattice by a shearing movement parallel to the first plane.

These ideas evidently have no application to the process that leads to the formation of the Widmanstätten figures in the copper-silver system. The lattice types of the solvent and solute are the same; this condition precludes any unique matching of separate planes in the two lattices. Planes of the same index differ by a constant amount, namely, by about 10 per cent, and there are no planes of differing index that show even a

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<sup>27</sup> Fig. 11 in reference of footnote 2.

reasonably close similarity. The identity in lattice types between solvent and solute might suggest a behavior analogous to that observed for the precipitation of gamma from beta brass in which the lattices are nearly identical<sup>28</sup> and where simple polyhedrons were observed, as if the lattice of  $\beta$  brass transformed bodily, in three dimensional blocks. There is, however, a far greater difference in atomic volume between solvent and solute in the copper-silver system than between those in the copper-zinc system, and this may be considered as a serious departure from strict similarity in the two cases. No reasonable prediction concerning the nature of the Widmanstätten figure in this system seems possible.

Despite the lack of what has been assumed to be the necessary conditions for the formation of precipitated plates, both the copper-rich and the silver-rich alloys form well defined Widmanstätten figures of the plate type, lying accurately parallel to low index planes in the parent solid solution. Surprisingly, it is found that these plates lie parallel to different planes in the two series of alloys, to the  $\{100\}$  in copper-rich and the  $\{111\}$  in silver-rich. Even more unexpectedly it is found that the orientation of the lattices of the precipitate in both cases is identical with that of the parent solid solution. This identity in orientation between parent solid solution and precipitate, on the basis of present theory, would alone preclude the formation of plate structures, yet these form with pronounced crystallographic precision and, furthermore, select different planes in the two series of alloys.

It appears, therefore, that the close matching of atom planes is not a necessary condition for the formation of plates, and that when this condition is absent a mechanism of nucleation and growth other than the one postulated becomes operative, a mechanism not related to the simple lattice geometry of the matching of atom planes but determined by other factors. Nucleation should be easier when the simple transformation of atom planes is possible and more difficult when this is impossible. The first might well be thought of as a process of easy self-inoculation. The reluctance of the copper-silver system to develop Widmanstätten figures and its preference to form rather ill-defined pearlite-like structures points to the absence of a readily operative mechanism for the formation of the figure. It is quite possible that the many anomalies shown by the precipitation process in this system may be determined by the operation of an unusual type of atomic precipitation mechanism.

The pearlite-like microstructure is unusual in precipitating alloys. Apart from the mode of distribution of the two constituents in the decomposed alloy, the growth of areas at the grain boundaries and of

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<sup>28</sup> R. F. Mehl and O. T. Marzke: Studies upon the Widmanstätten Structure, II—The  $\beta$  Copper-zinc Alloys and the  $\beta$  Copper-aluminum Alloys. *Trans. A.I.M.E.* (1931) **93**, 123.

spheroids within the grain, as observed by Norbury, also associates the structure with that of pearlite. In the formation of pearlite also the matrix decomposes without gradually changing composition of the parent solid solution. This analogy may be purely adventitious but is none the less striking. It is interesting to note that W. P. Sykes<sup>29</sup> observed very similar structures in cobalt-tungsten alloys; his Fig. 33 is very similar to Fig. 4, which shows the pearlite-like structure. This same cobalt-tungsten alloy when heat-treated differently developed a very well defined Widmanstätten type of structure, much as in the present case. It may be confidently predicted that only the initial and final values of the lattice dimensions of the parent solid solution will be found in the decomposition of these alloys also.

There appears to be no theory to offer to explain the structures observed in this system. Factors controlling crystal habit might well be considered, but none seems pertinent or useful. It is possible that differences in diffusion velocity along different crystal axes in the matrix might in one case grow plates upon one plane and in another upon another plane, but the isometric character of the lattices involved seems to weaken such an argument. To be sure, the electron structures of copper and silver differ somewhat, but this difference offers little hope of reasonable inference. It is, of course, quite possible that solute atoms arranged on certain planes in the matrix are inherently more prone to separation than those arranged on other planes, that is, less soluble in a thermodynamic sense much as atoms on different planes display different vapor pressures, but this is an unexplored possibility that offers no help at present.

#### SUMMARY

1. A Widmanstätten figure may be formed in copper-rich copper-silver alloys by extremely slow cooling. The silver-rich precipitate takes the form of plates parallel to {100} planes of the copper-rich matrix.

2. The precipitate in silver-rich copper-silver alloys is usually a pearlite-like arrangement of irregular plates. By extremely slow cooling a Widmanstätten figure may be developed in which the copper-rich precipitate forms plates parallel to the {111} planes of the matrix.

3. X-ray data prove that there is an identical orientation of matrix and precipitate lattices in the copper-rich alloys. The same is true of the silver-rich alloys even when the outward form of the precipitate is like pearlite in appearance.

4. Previous theories for the mechanism of formation of Widmanstätten figures fail to explain these results. It is suggested that the usual

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<sup>29</sup> W. P. Sykes: The Cobalt-tungsten System. *Trans. Amer. Soc. Steel Treat.* (1933) **21**, 385.

mechanism is not operative and that a less frequent mechanism is involved. The nature of this mechanism is not known.

5. Numerous grains in silver-rich alloys, when quenched and annealed, recrystallize into a new set of orientations related to the orientation of the original grain. The new orientations may be derived from the original by rotations in two directions of  $42^\circ \pm 5^\circ$  about [100], [010] and [001] directions of the original lattice as axes. The recrystallization appears to be associated with the discontinuous change of matrix lattice dimensions during precipitation.

#### ACKNOWLEDGMENTS

We are indebted to Mr. R. A. Lincoln, of the Carnegie Institute of Technology, for help in the preparation of some of the photomicrographs and X-ray photograms, and to Dr. Cyril Stanley Smith, of the American Brass Co., Waterbury, Conn., for his gift of one of the alloys used in our preliminary studies.

#### DISCUSSION

(*W. P. Sykes presiding*)

C. H. SAMANS,\* Bethlehem, Pa. (written discussion).—It is unfortunate that such an interesting and important paper should give results that are not in accord with the usual mechanism for the formation of Widmanstätten figures. Naturally, without a considerable amount of experimental work, it would be practically impossible to show that any special theory was correct. However, a possible path seems to be indicated by some coincidences in the behavior of the three metals copper, silver and gold when alloyed with one another. The dangers of reasoning by analogy in such a case are great, as frequently results are more apt to be in error than to be correct. However, if, as seems to be true here, no other solution to a problem is at hand, this method may often assist in at least indicating a path toward a correct explanation.

The metals copper, silver and gold, while behaving quite similarly chemically, display among themselves many points of metallurgical dissimilarity. Gold dissolves both silver and copper in any amount. Apparently, from the lack of superlattice formation, this solution takes place by a perfectly random substitution of copper or silver atoms for the gold atoms in the solvent lattice. Silver dissolves gold in all proportions and copper to a limited extent. No signs of any superlattice formation having been found in the silver-gold alloys, it might be said that here also the solution takes place by a random substitution of atoms and, reasoning by analogy, it might be thought that copper would also dissolve in the silver lattice by random substitution, the difference in solubilities being attributable to some as yet unknown atomic factor. Copper, on the other hand, differs in its solvent action. While it dissolves gold in all proportions, the gold atoms, at least under the proper conditions, seem to have a preference for substituting for definite atoms in the copper lattice. This is evidenced by the formation of the compound  $\text{Cu}_3\text{Au}$ , in which the gold atoms occupy the corner positions and the copper atoms the face-centered positions. This, then, might be considered as a superlattice instead of a compound if one so desired. Again reasoning by analogy, it might be said that there is at least a possibility of a similar tendency

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\* Instructor, Department of Metallurgical Engineering, Lehigh University.

toward the formation of such a superlattice in the copper-rich copper-silver alloys. That such a phenomenon has not been reported is not at all extraordinary, considering the similarity of the atoms involved, and the absence of a specific search for it.

Let us consider now the significance of the arrangements of these atoms if they could be actually proved to occur. In the silver-rich solid solution, the copper atoms would replace silver atoms in a random manner to a maximum of 14 atomic per cent (roughly,  $\frac{1}{4}$  of the total number of atoms present). If precipitation is to occur in discrete areas throughout the matrix, there must be regions in which atoms of the same kind—i.e., copper atoms—occur together. The laws of probability would practically require this to take place on the closest packed, octahedral planes. Heat-treatment, by increasing the tendency toward diffusion, would cause a further aggregation of copper atoms along these planes. As long as they can remain in solution, they will do so. However, when the temperature falls to such an extent that the composite lattice is no longer stable, the copper atoms might be expected to separate from the silver matrix in an abrupt manner because of the differences in the size of their molecules. Since the copper atoms originally were on octahedral planes in the solid solution lattice, it might be expected that the (111) planes in the new lattice would continue to remain parallel to these planes after precipitation. Further stages in the process would be merely repetition of the above, accompanied by the aggregation of the precipitated materials into larger particles.

In the copper-rich solid solution circumstances would be somewhat different. Copper will dissolve silver to a maximum of 4.3 atomic per cent. If, as we assumed above, these silver atoms prefer to substitute for the corner atoms of the copper lattice, then, roughly,  $\frac{1}{8}$  of the corner atoms could be occupied by silver atoms. This would probably mean that the cube planes would include a larger number of silver atoms than the other planes in the lattice. As a consequence of this, when precipitation occurred, the new lattice (silver) might be expected to have its cube planes parallel to the cube planes of the matrix because they were in this position before precipitation.

The three distinct hardness maxima reported by Wiest could then be explained by: (1) the tendency of the solid atoms to arrange themselves in the corner positions, producing a strained lattice, but with no appreciable change in lattice dimensions; (2) the actual precipitation process, producing hardening effects by the keying action of the precipitating materials as well as by the disarranged matrix of the material resulting from the precipitation; (3) the final diffusion of the remaining silver atoms to the precipitated particles and their conglomeration, again producing a strained matrix.

Naturally these few isolated facts which, by coincidence, have seemed to fall together into a very loose explanation of the precipitation process in these alloys cannot carry much conviction because definite proof is lacking. Indeed, it would seem more than probable that the thought has already occurred to the authors and been rejected as unfeasible because, owing to their larger experience with alloys of this type, many points must be known to them with which the writer is unfamiliar. However, as a possibility that has not heretofore been brought out, it may contain a few points of merit and it would seem that a study of the silver-copper alloys made along the lines of that of Bradley and Jay<sup>30</sup> on the iron-aluminum alloys would give specific information as to the possibility of superlattice formation in the copper-rich copper-silver solid solutions.

For lack of satisfactory X-ray equipment, the writer is unable to carry the work farther. Frequently, also, much better results in this field can be secured by men

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<sup>30</sup> A. J. Bradley and A. H. Jay: The Formation of Super Lattices in Alloys of Iron and Aluminum. *Proc. Roy Soc.* (1932) 136A, 210.

like Dr. Barrett and Dr. Mehl, who are undoubtedly experts in the use of the X-ray.

C. S. BARRETT (written discussion).—Any line of thought deserves consideration that has any promise of explaining the peculiar relations in this system (which we have summarized in two diagrams, Figs. 18 and 19).

Our experiments reported in the section on Powder Diffraction Spectra failed to produce any superlattice lines, and to judge from observations on other cubic systems it is unlikely that any could be found below about 12 atomic per cent. Nevertheless,

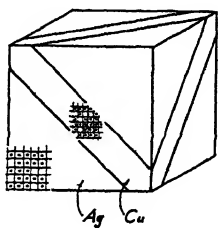


FIG. 18.

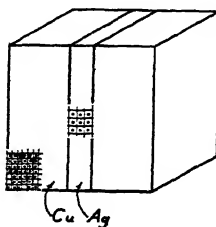


FIG. 19.

FIG. 18.—POSITION OF COPPER-RICH PLATE IN SILVER MATRIX; ALSO ORIENTATION OF LATTICES.

FIG. 19.—POSITION OF SILVER-RICH PLATE IN COPPER MATRIX; ALSO ORIENTATION OF LATTICES.

in the absence of positive evidence of a disordered arrangement in the solid solution under all conditions, we should not discard the idea of an ordered arrangement, since a degree of order that is insufficient to be revealed by new diffraction lines might still be able to effect the precipitation mechanism.

There is some uncertainty about the role that would be taken by a superlattice of the type postulated by Dr. Samans. We cannot agree that the superlattice would locate more silver atoms on cube planes than on any other planes, for planes of any index whatever include all atoms. No plane is favored according to this point of view. If, on the other hand, we consider the average density of silver atoms on the atomic planes of different index, the postulated superlattice would make the density greater on the octahedral planes than on the cube planes, and again we have a theory without merit. But if we consider only those cube planes that are assumed to contain silver atoms and neglect the alternate ones that contain none (in the completely ordered state), the cube planes would have a greater number of silver atoms per unit area than the octahedral planes (which are all alike). A nucleus of silver-rich precipitate might then be thought of as taking its external form from a high-density region of one of these cube planes. How much value there is in such speculation can hardly be determined from existing data.

We should like to report some additional data, obtained after the paper went to press, which strengthens our proof that the precipitate in the silver-rich alloys forms

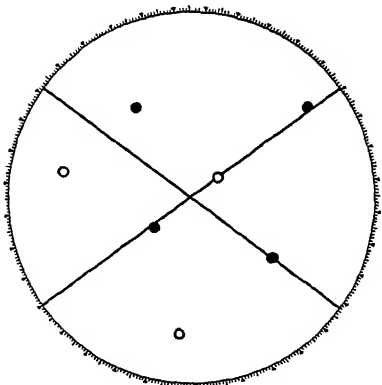


FIG. 20.—ORIENTATION OF A GRAIN, DETERMINED BY X-RAYS, OF COPPER ALLOY SHOWN IN FIG. 6.

on  $\{111\}$  planes. A large grain of the 4 per cent copper alloy shown in Fig. 6 was found to have well defined precipitate traces at angles different from those usually found, and at angles more favorable to a differentiation between  $\{111\}$  and  $\{100\}$  planes. The orientation of the grain, determined by X-rays, is represented in the stereographic projection of Fig. 20 by open circles for  $\{100\}$  poles and full circles for  $\{111\}$  poles. The normals to the trace directions, plotted as diameters on the projection, can be explained on the basis of precipitation on  $\{111\}$  planes alone, but not  $\{100\}$  planes alone, confirming our conclusions in the paper

## Determination of Orientations of Metallic Crystals by Means of Back-reflection Laue Photographs\*

BY ALDEN B. GRENINGER,† JUNIOR MEMBER A.I.M.E.

(New York Meeting, October, 1934)

MANY recent contributions in the field of theoretical metallography have been concerned with crystallographic definitions or descriptions of various phenomena. The lattice orientation of the crystal being studied must be known before such definitions can be made. Practically all the metallic crystals used do not have crystal faces—other than the unknown “plane of polish”; hence resort must be had to other means of determining orientations. Some use has been made of etch-figures, slip bands, optical properties, etc., for this purpose; but for accurate results, and because of the fewer restrictions to their use, the various X-ray methods have been the most satisfactory.<sup>1</sup>

The methods that have been used may be divided into two general classes: (1) oscillation methods, and (2) transmission Laue methods.<sup>2</sup> The disadvantages of these methods are numerous, chief among them being the time required to determine a complete orientation. No method proposed so far is wholly satisfactory for determining the orientation of a small macrograin within a polycrystalline aggregate.

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\* Part of a thesis to be submitted to the Graduate School of Engineering of Harvard University, in partial fulfillment of the requirements for the degree of Doctor of Science. Manuscript received at the office of the Institute Sept. 20, 1934.

† Graduate Student, Harvard University, Department of Metallurgy, Cambridge, Mass.

<sup>1</sup> Most of the work in developing X-ray methods for determining orientations, and in the application of these methods, has been done in Europe and Japan. The literature on this subject is too extensive to be included in this report. See, however, T. A. Wilson: A Study of Crystal Structure and Its Application, XII. *Gen. Elec. Rev.* (Nov., 1928) 31, 612 et seq. Wilson lists and discusses methods published prior to 1928. For later publications, see R. W. G. Wyckoff: *The Structure of Crystals*, bibliography at end of text.

<sup>2</sup> To avoid confusion the term “transmission Laue” will, in this report, refer to the well-known Laue method of crystal analysis. The back-reflection Laue method has apparently received little attention, in spite of its potentialities in the study of metallic crystals. Two short publications discussing its application to crystal analysis are by Von L. Chrobak [Die “Zurückreflektierten” Laue Interferenzbilder. *Ztsch. f. Krist.* (1932) 82, 342–347]; and W. Boas and E. Schmid [Laue-Diagramme mit grossen Ablenkungswinkeln, *Metallwirtschaft* (Dec., 1931) 10, 917–919. Abst. in *Metals & Alloys*, April, 1933].



The back-reflection Laue method offers a simple, rapid means of determining orientations. All problems involving cubic crystals may be solved with only one photograph, which can be taken in two or three hours and interpreted in a few minutes. The technique which the author is using at present gives an accuracy of at least one-half degree, which is about the limit of accuracy of stereographic or gnomonic plotting.

This method is based on the fact that, in an "unsymmetrical" pattern, a quasisymmetrical arrangement of spots is maintained to an extent that readily permits the identification (from visual inspection) of important diffraction spots. After one has become familiar with the symmetrical back-reflection diagrams of the cubic system,<sup>3</sup> the diffraction spots from  $\{100\}$ ,  $\{110\}$  and  $\{111\}$  planes (and certain other planes) can be identified for practically any position in which they may occur on a photograph.

### GENERAL DISCUSSION

The basic scheme of the back-reflection Laue method is illustrated in Fig. 1. A beam of white X-radiation, limited by a suitable pinhole system (the third hole is a small lead cylinder), passes perpendicularly through a hole in the photographic film, strikes the crystal, and is diffracted back to the film  $F$ , each important atomic plane, such as  $P$ , selecting the correct wave length to give a diffraction spot according to the fundamental equation  $n\lambda = 2d \sin \theta$ . The reflection angle  $\phi$  in Fig. 1 is equal to  $180^\circ - 2\theta$ .

Because of geometrical dissimilarities of diffraction in the transmission Laue and back-reflection Laue methods, the resulting patterns are quite different. In the symmetrical transmission Laue photograph, the Laue spots lie on elliptical tautozonal curves which pass through the central point of the pattern; the tautozonal straight lines, which may be drawn, also pass through the center. In back-reflection Laue photographs the tautozonal curves are hyperbolas or straight lines; the former do not pass through the center, but the latter do.

The origin of the hyperbolic pattern is illustrated in Fig. 2. An X-ray beam, passing through a photographic film at  $O$ , strikes the crystal at  $C$ , which is symmetrically oriented with respect to the incident beam and vertical axis  $LO$ , and gives a diffraction spot (considering only one of the many spots obtained) at  $L$  on the photographic film. The plane producing this diffraction spot lies in the zone of which  $BC$  is the zone axis. Let line  $CL$  rotate about point  $C$ , keeping angle  $LCB$  constant.  $CL$  will then describe a cone in space, the axis of the cone being  $BC$ ,

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<sup>3</sup> The writer so far has applied the method only to crystals of the cubic system. However, it should be applicable to the study of metallic crystals of lower symmetry as well.



perpendicular to the line bisecting angle  $OCL$  and lying in the plane  $LEO$ . The base of this cone (a circle), centrally projected on to the photographic film from point  $C$ , describes the hyperbola  $KLM$ . All diffraction spots from planes lying in the zone of which  $BC$  is the zone axis will lie on the

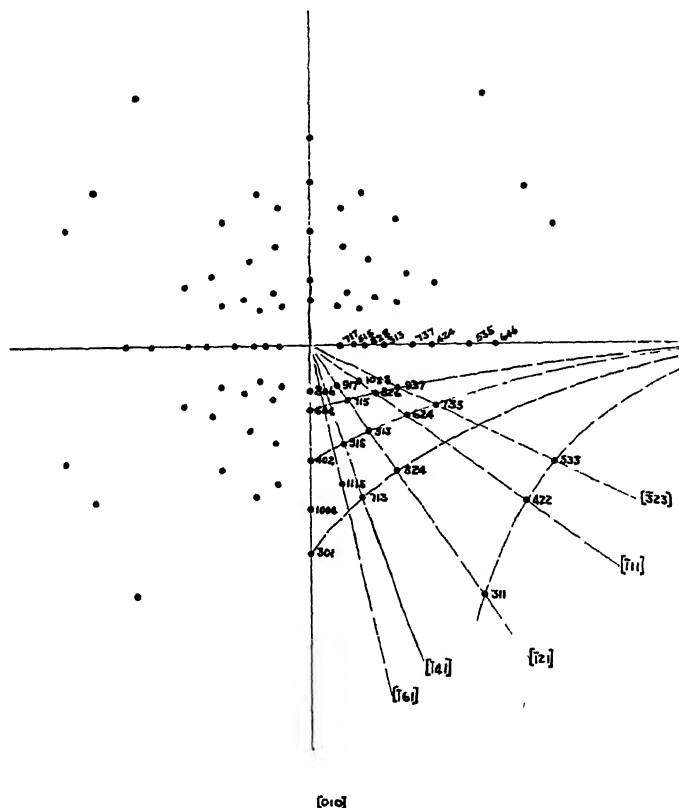


FIG. 3.—DIAGRAM OF BACK-REFLECTION LAUE PATTERN FOR FACE-CENTERED CUBIC CRYSTAL OF COPPER, WITH INCIDENT BEAM OF X-RAYS PARALLEL TO TWOFOLD AXIS. CRYSTAL-TO-FILM DISTANCE, 3 CM. (REDUCED ABOUT ONE-THIRD.)

tautozonal curve  $KLM$ . It is readily apparent that the dimensions of line  $CO$  and the angle  $OCL$  determine the location of the hyperbola  $KLM$ . It is possible, therefore, to construct graphically<sup>4</sup> plats of prominent tautozonal curves for different symmetrical orientations of the crystal with respect to the photographic film; if a fourfold axis of symmetry of the crystal is normal to the film, the hyperbolic pattern will have fourfold symmetry. Plane indices can be determined by the usual method of cross multiplication (method of determinants) of zone symbols.

<sup>4</sup> This construction is greatly facilitated by using the hyperbolic angular-coördinate plat described later in this paper.

The writer used this method to obtain diagrams of the spots to be expected with the X-ray beam normal to a  $\{100\}$ ,  $\{110\}$  and  $\{111\}$  plane of a face-centered cubic crystal before any symmetrical photographs had been taken. Naturally, the accuracy of the final result is dependent

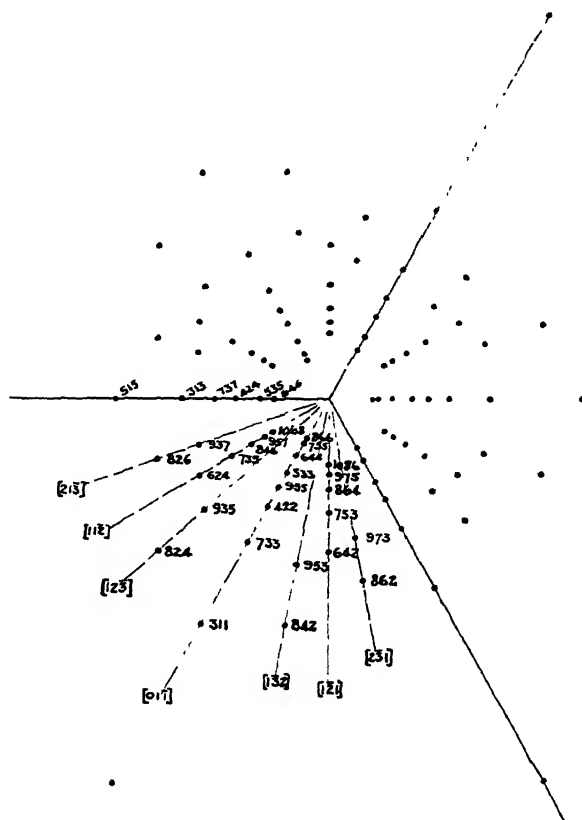


FIG. 4.—BACK-REFLECTION LAUE PATTERN OF COPPER, WITH INCIDENT BEAM OF X-RAYS PARALLEL TO THREEFOLD AXIS. CRYSTAL-TO-FILM DISTANCE, 3 CM. (REDUCED ABOUT ONE-THIRD.)

on the care taken in the graphical construction. Once the approximate locations and the indices of the diffraction spots are known, they may be located exactly through the use of the well-known equation for the angle between two planes  $(hkl)$  and  $(h_1k_1l_1)$  in the cubic system:

$$\cos \alpha = \frac{hh_1 + kk_1 + ll_1}{\sqrt{h^2 + k^2 + l^2} \cdot \sqrt{h_1^2 + k_1^2 + l_1^2}} \quad [1]$$

Figs. 3 and 4 show the spots obtained from a face-centered cubic crystal when the X-ray beam is parallel to a twofold and a threefold axis of symmetry, respectively. The distance from film to specimen in

both cases is 3 cm. A study of these two diagrams will show why the back-reflection Laue method is so useful in determining orientations. The hyperbolic tautozonal curves in the (101) diagram become the tautozonal straight lines in the (111) diagram. In an unsymmetrical

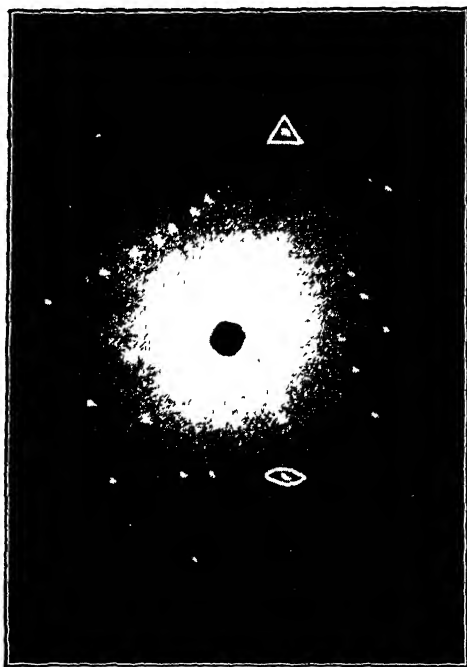


FIG. 5.—UNSYMMETRICAL BACK-REFLECTION LAUE PHOTOGRAPH OF NUCLEUS OF COPPER CRYSTAL.

The spot marked by a triangle =  $\{111\}$ , the one marked by an oval =  $\{101\}$ .

diagram, with the X-ray beam perpendicular to some plane between  $\{101\}$  and  $\{111\}$ , these tautozonal curves remain hyperbolas, easily identifiable. Such an unsymmetrical photograph is shown in Fig. 5, in which a  $\{111\}$  spot and a  $\{101\}$  spot<sup>5</sup> are readily apparent. One photograph such as that illustrated in Fig. 5, with two identified spots, is all that is needed for a complete plot of the orientation of the crystal.

The general form of the indices of spots obtained in the two Laue methods is different. In a transmission Laue pattern in which the  $z$  axis coincides with the incident X-ray beam, all spots obtained are diffractions

<sup>5</sup> In transmission Laue photographs, first-order diffracting accounts for most of the intensity of each spot. In back-reflection Laue photographs, most spots are of first-order diffraction, but the salient diffraction order of the important spots,  $\{100\}$ ,  $\{101\}$ ,  $\{111\}$  and certain others, may range as high as 10 or more, depending upon the experimental conditions, orientation of the crystal, etc. Thus, for face-centered cubic crystals, we obtain intense diffraction spots from  $\{100\}$  and  $\{110\}$  planes, for though of high order, the intensity is usually greater than that of the neighboring first-order diffraction spots of high indices.

from planes of the form  $(hkl)$ , or from planes which can be reduced to that form. Under the same conditions, a back-reflection Laue pattern contains spots which, expressed in terms of intercepts, are of the form

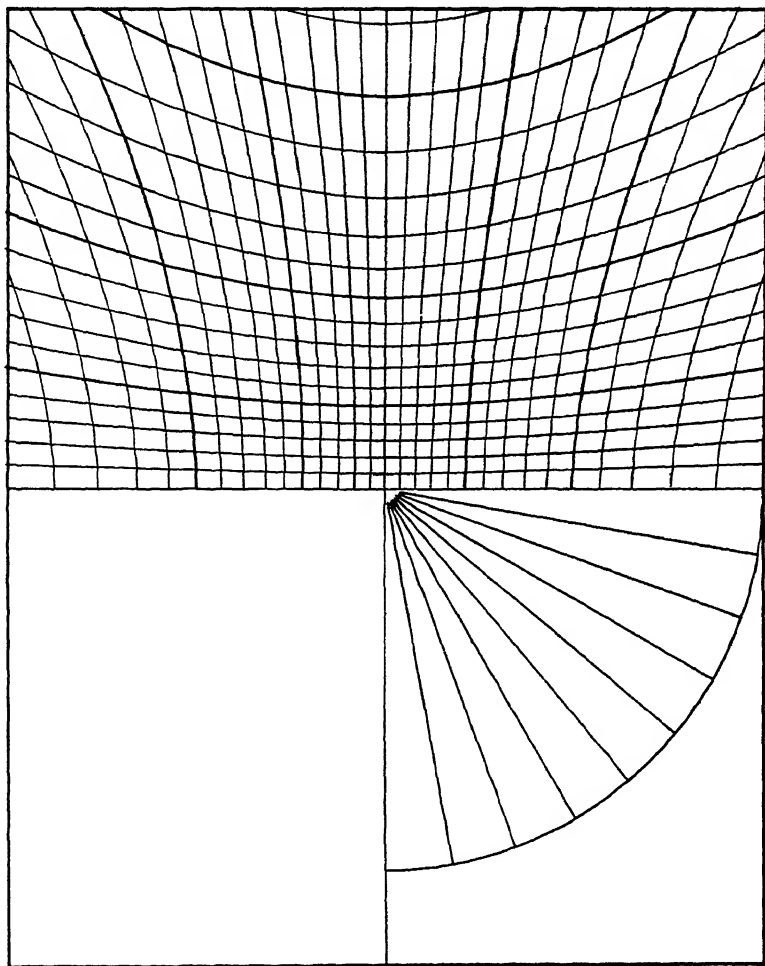


FIG. 6.—HYPERBOLIC ANGULAR-COORDINATE PLAT (UPPER HALF), FOR CRYSTAL-TO-FILM DISTANCE OF 3 CM. FOURTH QUADRANT IS DIVIDED CIRCULAR ARC. FULL SIZE.

(*ab1*). When gnomonic projection is applied to back-reflection Laue photographs, the resulting coordinate system is not uniform but logarithmic in character. A projection in terms of intercepts is simpler to make.

#### CONSTRUCTION OF A HYPERBOLIC ANGULAR-COORDINATE PLAT

The orientations of unsymmetrical back-reflection Laue diagrams are very rapidly solved through the use of a coordinate plat, such as that

illustrated in Fig. 6, used as a positive on a photographic film. In this plat, both horizontal and vertical parallels are hyperbolas, located  $2^\circ$  apart, and give the angular coordinate of a Laue spot (with respect to the vertical or horizontal) in terms of the angles made by the diffracting plane with the vertical, or horizontal, or any reference line that is chosen on the crystal surface.

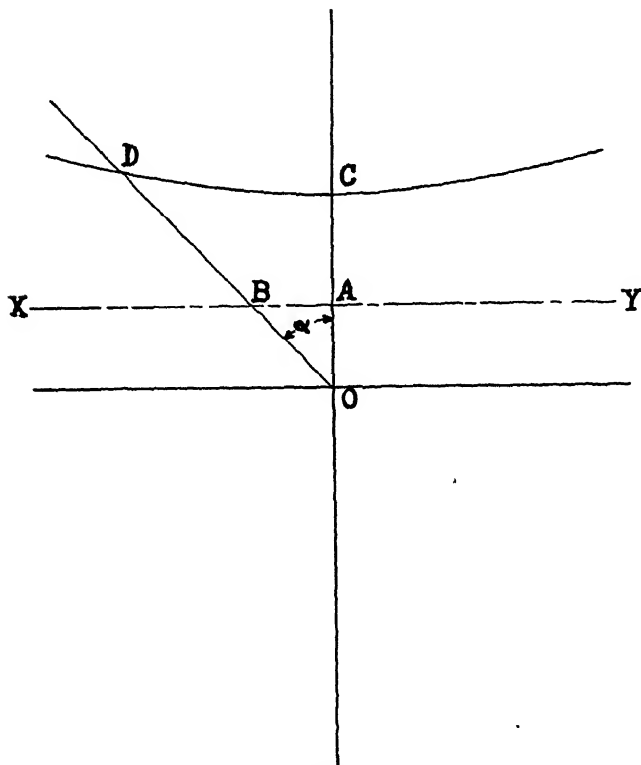


FIG. 7.—CONSTRUCTION OF HYPERBOLIC ANGULAR-COORDINATE PLAT.

Possibly the simplest and most accurate method of constructing such a plat is to use a system of plotting on lines radiating from the origin at definite angles with the horizontal (or vertical).

In Fig. 7 (on the plane of the photographic film) the X-ray beam is considered as passing perpendicularly through the plane of the drawing at  $O$ , striking a crystal at  $R$  distance from  $O$ , and being diffracted back to produce two spots  $C$  and  $D$ .  $C$  is on the vertical axis and  $D$  is any point tautozonal with  $C$ . Then, let  $\phi$  = the reflection angle for point  $C$  (the angle between the incident X-ray beam and the diffracted beam); similarly,  $\phi_1$  = the reflection angle for point  $D$ .  $XY$  is the locus of the gnomonic projection of the imaginary diffracting plane as the plane is

rotated about an axis which is the intersection of the vertical plane through  $O$  and the diffracting plane.

$$\text{Then, } \tan \frac{\phi_1}{2} = \frac{OA}{R \cos \alpha} \quad [2]$$

$$\text{And } OD = R \tan \phi_1 \quad [3]$$

(Four or five points such as  $D$  on each hyperbola are sufficient for a complete plot of each hyperbolic coordinate line.)

### USE OF THE HYPERBOLIC COORDINATE PLAT

In order that a complete plot of the orientation of a crystal may be made, it is necessary to obtain the angular coordinates with respect to some reference line on the crystal, of either: (1) two back-reflection Laue spots which are easily identified on the photograph, or (2) one identified Laue spot and one identified tautozonal curve.<sup>6</sup> This identified curve will practically always be a curve passing through the identified Laue spot.

When two Laue spots can be identified, the coordinate plat is placed over the photograph, with the horizontal of the plat corresponding with the horizontal of the photograph if the reference line on the crystal is either horizontal or vertical. The angular coordinates of the spots are then read directly from the plat. The coordinates can then be transferred to a stereographic projection. The angle between the two poles on the projection, measured with a stereographic net, offers a check for the correct identification of the two Laue spots.

When one Laue spot and a zonal curve are identified, the angular coordinates of the Laue spot are determined as before; then the coordinates of any unknown spot on the curve are determined and plotted stereographically. The positions of the unknown pole and the known pole on the stereographic projection determine the position of the tautozonal curve on that projection. Having, then, one known pole and a known zonal curve, the projection of the desired cubic forms may be completed by the ordinary stereographic methods.

The hyperbolic plat may be used as an aid in identifying spots in the photograph, inasmuch as the angle<sup>7</sup> between two planes ( $hkl$ ) and ( $h_1k_1l_1$ ) which produce two spots on a back-reflection photograph may be read directly from the plat in much the same way as the angle between two poles on a stereographic projection may be measured with a stereographic net. Likewise, the angle<sup>7</sup> between two zone axes [ $uvw$ ] and [ $u_1v_1w_1$ ] producing two intersecting zonal curves on the film may be read from the plat, and thus facilitate the assignment of symmetry characteristics to a spot or curve.

<sup>6</sup> The third case—the identification of two intersecting zonal curves without any identified Laue spots—will seldom, if ever, be encountered in unsymmetrical photographs.

<sup>7</sup> Approximately only. A simple calculation will give the exact value.



To measure the angle between two spots, the plat is placed over the photographic film, with centers coinciding, and rotated until a hyperbolic parallel coincides with the zonal curve connecting the two spots in question. The angle between the two spots (between the planes producing them) is then read directly from the other set of parallels. This angle should correspond with the angle given by equation 1.

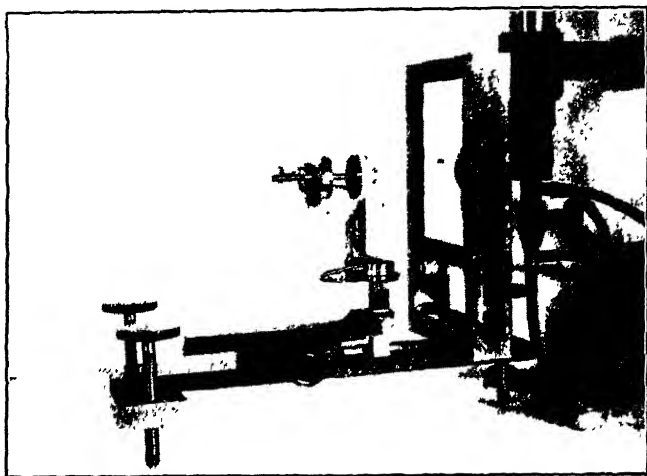


FIG. 8.—BACK-REFLECTION LAUE CAMERA, MOUNTED IN FRONT OF X-RAY TUBE.

To measure the angle between two curves, the plat is placed over the film with centers coinciding so that a parallel coincides with one of the zonal curves. The plat is then rotated until another parallel coincides with the other zonal curve in question; the angle of rotation of the plat, measured by means of the radial lines on the plat, gives the angle between the zone axes producing the two zonal curves.<sup>8</sup>

#### THE BACK-REFLECTION LAUE CAMERA

For any extended use of the back-reflection Laue method, it is desirable to have a suitable goniometer for making controlled reorientations of the crystal to be studied. A camera equipped with a special type of three-circle goniometer (constructed for the writer by the Mann Instrument Co., Cambridge) is shown in Fig. 8.

When the condition occurs in which no Laue spots can be identified on a photograph with certainty, the specimen is rotated through a known angle and another photograph is taken. It is seldom necessary to take more than two photographs. Occasionally it is desirable to check the identification of a Laue spot, by reorienting the crystal to

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<sup>8</sup> Approximately only. A simple calculation will give the exact value.

bring the spot in question to the center of the diagram. However, one photograph properly interpreted will always establish the orientation of a cubic crystal.

#### GENERAL REMARKS ON THE BACK-REFLECTION LAUE METHOD

This method has its greatest usefulness in the study of materials which are opaque to X-radiation; i.e., most metallic crystals. In most of these crystals, diffraction takes place within a relatively thin surface layer of the crystal. The approximate relative penetration for each Laue spot of known indices may be calculated from absorption coefficients. The method can be applied to the study of transformations which occur on surfaces but do not extend to any considerable depth.

The most desirable type of X-radiation for back-reflection photographs is moderate-voltage tungsten radiation (about 30,000 volts). However, radiation from copper, iron, or chromium targets is satisfactory, though not as efficient, if the characteristic rays from these targets are effectively screened out. For determining orientations the use of an intensifying screen is desirable. As in the transmission Laue method, precautions must be taken to filter as much as possible of the secondary X-radiation emitted by the crystal. For metals such as copper, zinc, iron, etc., this radiation consists largely of soft X-rays which can be screened quite effectively; for copper, the writer has used 0.010 in. of aluminum placed in contact with the photographic film.

For determining orientations, most back-reflection Laue photographs are taken with a specimen-to-film distance of 3 cm. When this radius and a 4 by 5-in. film are used, an angular range of about  $60^\circ$  is covered by the film.

#### ACKNOWLEDGMENT

The writer wishes to express his appreciation to Dean H. E. Clifford and the Harvard Engineering School for facilities and aid which are making this research possible, and to thank Dr. H. H. Lester, lecturer on X-ray analysis at Harvard University, and Prof. M. J. Buerger of Massachusetts Institute of Technology, who read the manuscript and suggested certain revisions.

#### DISCUSSION

(*G. E. Doan presiding*)

L. W. McKEEHAN,\* New Haven, Conn.—The author mentions that it is a great advantage, in fact, sometimes necessary, to have a filtering screen between the crystal and the film. The reason that is necessary here and is not necessary in back-reflection powder photographs, is worthy of note. In a powder photograph a ring that makes a small angle with the forward beam and a ring that makes the same

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\*Director, Sloane Physics Laboratory, Yale University.

angle with the backward beam will be not very different in intensity. But a Laue spot that makes a small angle with the forward beam is much more intense than one that makes this angle with the backward beam. The equations that bring that to our attention are given perhaps most completely by Mark, in his book on the application of X-rays in chemistry and technology, written some years ago.

The point is that if we plot the intensity, or the brightness of the portion of a powder ring, as a function of the glancing angle (which can run from zero to  $90^\circ$ ) the curve is something like that shown in Fig 9, having its minimum near the glancing angle of  $45^\circ$  but rising again, for a very perfect crystal, with no heat motion, much higher than that. In the case of a Laue spot, which may arbitrarily be taken as having the same intensity at a small angle of deviation, the corresponding curve does not rise so much after passing the minimum and the advantage of the back-reflection method is lost in recondensing the diffraction into a small area.

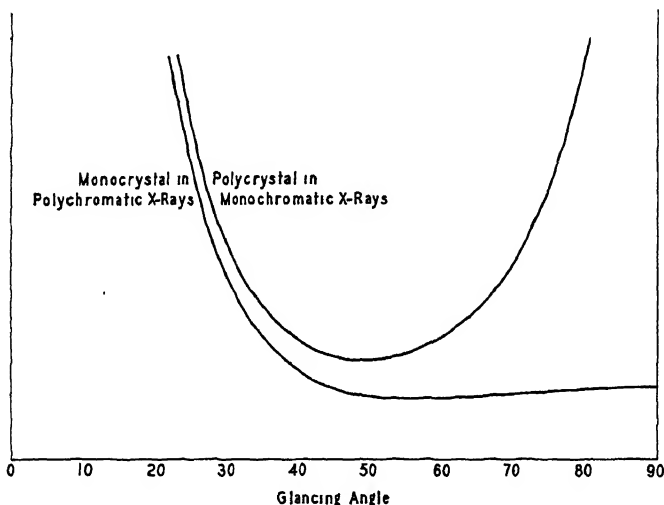


FIG. 9.—COMPARISON OF INTENSITIES FOR TWO METHODS OF CRYSTAL ANALYSIS.

No account has been taken of atomic structure factor or heat motion, both of which diminish intensity at larger glancing angle.

I received a copy of the manuscript of this paper some time ago, and Mr. Elmore, working in our laboratory, has been able to try out the method in studying the orientation of some iron and nickel single crystals with respect to a polished surface. The crystals that we were working with were polished and had, of course, some broken microcrystalline material on the surface. In that condition, the powder pattern of that broken-up material with white radiation would give a considerable intensity, spread out, of course, in the region of the back reflection. The use of a thin aluminum foil was competent to cut down this stray intensity, which is of a fairly long wave length on the average, very markedly, whereas the Laue spots, which were interesting in determining the symmetry, were, as the author also points out in the paper, frequently of very high order and always dependent for a great deal of their intensity upon the short-wave radiation from the target.

There have been a few photographs of this kind in the literature. In the paper itself the author refers to two or three places where such photographs appear in German publications. I can add to these one reference, which recently came to my attention. Schmid and Siebel, in *Metallwirtschaft* of May 18, 1934, give such a back

Laue picture of a magnesium cleavage face, which shows the sixfold symmetry about the normal very clearly indeed.

All that has been said about the convenience of the method is true. It is very easy to apply and the results compare most favorably with the more standard methods of repeated exposures at different positions which frequently have been used in applying the Bragg method to finding the orientation of a crystal fragment.

H. H. LESTER,\* Watertown, Mass. (written discussion).—Back-reflection Laue patterns should be applicable to the study of crystallites in position in polycrystalline metal. There is need for such study. Physical metallurgy is more and more concerned with irregularities in crystallinity, with relative orientations within individual grains, with changes in orientation due to plastic deformation or other causes, with various other structural peculiarities in which orientations may be involved. Back-reflection diffraction patterns have not been used extensively for such studies, partly at least because of difficulties of analysis. Dr. Greninger offers a method that is simple and positive and should make the handling of a back-reflection picture of no greater difficulty than that of the ordinary Laue.

C. S. BARRETT,† Pittsburgh, Pa. (written discussion).—Mr. Greninger has developed a method of determining crystal orientation that should be particularly useful for small grains or for small regions of large crystals. A limitation of the method should be mentioned, however; it does not seem to be a suitable method for dealing with superimposed diffraction patterns; i.e., with simultaneous diffraction from grains of different orientations. Such problems may be encountered, for example, in Widmanstätten studies where one may obtain a diffraction pattern from a grain of a solid solution and simultaneous patterns from a number of differently oriented precipitated crystals lying within that grain. In such cases the relative orientation of matrix and precipitate can usually be determined if some orientation method is used that involves monochromatic radiation, for then the identity of each of the spots in the pattern can be obtained from its angle of diffraction. But in a Laue method, such as Mr. Greninger's, the diffraction angles cannot be used for the indexing of the spots or the identifying of the spots as coming from matrix or precipitate; the identification of the spots must rest upon the symmetry of the photogram, which would be confused by the many superimposed patterns.

A. B. GRENINGER (written discussion).—It is gratifying to find that Professor McKeehan has already adopted this method as a means for finding the orientations of iron and nickel crystals. Professor McKeehan has given a very clear explanation of one of the reasons for using a filtering screen between the crystal and film. Another reason (mentioned in the paper) for using the filter is the need for minimizing the effect of secondary radiation. It is fortunate, for this method at least, that the metallurgically important metals, iron, copper, zinc, nickel, etc., give secondary X-ray emissions of relatively long wave lengths, which can be filtered easily. As the atomic number of the metal increases, the spread between the wave lengths of the *K*-series emission and the useful portion of the primary beam decreases; the efficiency of filtering is lessened as this spread decreases. When one applies the back-reflection Laue method to metals of high atomic number, it is sometimes advisable to work with potentials below the *K*-series excitation limit of the metal, in order to obtain clear patterns.

Dr. Lester has mentioned the applicability of the back-reflection Laue method in the study of grains in polycrystalline metal. The method is well suited for such studies; orientation relationships of small macrograins (of sizes down to about 0.5 mm.)

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\* Research Physicist, Watertown Arsenal.

† Metals Research Laboratory, Carnegie Institute of Technology.

may be determined rapidly. In working with such material, it is not necessary to secure a pattern from each grain individually; orientation patterns from three or four adjoining grains may be obtained simultaneously on the same film, without complicating the solution a great deal.

It is certainly true, as Dr. Barrett has stated, that Widmanstätten studies present problems that are difficult to solve completely by any one X-ray method. In very few Widmanstätten problems, however, has it been possible to fix completely the orientation relationships of the phases involved. Dr. Barrett's work on the silver-copper system is an excellent example of a complete solution, facilitated by the presence of only one precipitate-orientation. Results that have been obtained from Widmanstätten studies by the method of pole figures are not really determinations or fixations, but only approximations—necessarily so because of the nature of the material that has to be studied. It is important, then, to differentiate between an actual *determination* of the orientation relationships of two or more grains (which may be done with a back-reflection Laue pattern with an accuracy of  $\frac{1}{10}$  degree or less, if this accuracy is needed), and an *approximation* of what may be a mean relation between a solid solution grain and a large number of precipitated crystals.

A word should be said regarding the hyperbolic coördinate plat illustrated in Fig. 6. Both sets of curves correspond to zone-axes projections and therefore to the great circles on a stereographic projection. A plat that could be used with *greater facility*, but which involves considerably more labor in its construction, is one with both parallels and meridians; that is, arranged according to the system of polar coordinates. A description of such a polar-coordinate plat together with tabulations of values for plotting the curves will appear in a forthcoming issue of the *Zeitschrift für Kristallographie*.

## Crystallographic Uniformity of Lineage Structure in Copper Single Crystals\*

BY ALDEN B. GRENINGER,† JUNIOR MEMBER A.I.M.E.

(New York Meeting, February, 1935)

THE study of mosaic structure of crystals<sup>1</sup> has been confined until recently to the field of theoretical physics. Crystallographers, in general, have neglected the subject, although X-ray crystallographers constantly make use of formulas for intensities of X-ray reflection as modified by mosaic structure.

Work on mosaic structure has centered chiefly on the task of proving or disproving the secondary-structure theory of Zwicky,<sup>2</sup> and very little attention has been paid to the visible imperfections of crystals. A. Goetz has been responsible for most of the supposed experimental confirmations of Zwicky's theory.<sup>3</sup> On the other hand, Smekal,<sup>4</sup> and Orowan,<sup>5</sup> among others, maintain that there is neither theoretical nor experimental evidence to substantiate Zwicky's secondary structure.

Lately the subject has been intensively investigated by Buerger,<sup>6</sup> one of whose recent papers led to a symposium on mosaic structures.<sup>7</sup>

\* Part of a thesis to be submitted to the Graduate School of Engineering of Harvard University in partial fulfillment of the requirements for the degree of Doctor of Science. Manuscript received at the office of the Institute Nov. 7, 1934.

† Graduate Student, Harvard Engineering School, Department of Metallurgy, Cambridge, Mass.

<sup>1</sup> A good summary of the subject is given by C. H. Desch [The Chemistry of Solids, chap. VI. Cornell Univ. Press, 1934.] For the most recent treatments of particular phases, see the various papers of the mosaic structure symposium in *Ztsch. f. Krist.* (1934) **89**, 193-416.

<sup>2</sup> See, for example, F. Zwicky: On the Physics of Crystals. *Rev. Modern Physics* (July, 1934) **6**, 193-208.

<sup>3</sup> For example, A. Goetz: On the Experimental Evidence of the Mosaic Structure of Bi Single Crystals. *Proc. Nat. Acad. Sci.* (1930) **16**, 99-105.

<sup>4</sup> A. G. Smekal: On the Theory of Real Crystals. *Phys. Rev.*, **44**, 308-309.

<sup>5</sup> E. Orowan: Bemerkung zu den Arbeiten von F. Zwicky über die Struktur der Realkristalle. *Ztsch. f. Physik* (1932) **79**, 573-582.

<sup>6</sup> M. J. Buerger: The Significance of "Block Structure" in Crystals. *Amer. Mineralogist* (1932) **17**, 177-191; The Lineage Structure of Crystals. *Ztsch. f. Krist.* (1934) **89**, 195-220; The Non-existence of a Regular Secondary Structure in Crystals. *Ztsch. f. Krist.*, (1934) **89**, 242-267.

<sup>7</sup> Reference of footnote 3, 1.

Buerger was the first investigator to apprehend the potential significance of the optical imperfections appearing in many natural and prepared crystals. His study of data secured from visual examinations and tests on these imperfections led to his formulating a general theory of the mechanism of crystal growth.

Lately, Buerger's lengthy critical examination of the evidence,<sup>8</sup> both theoretical and experimental, advanced by Zwicky and coworkers, resulted in a convincing demonstration of the crystallographic impossibility of the existence of single, periodic, submicroscopic secondary structure in crystals.

To avoid confusion, the following definitions of terms, as used by most crystallographers and physicists, are given:

*Mosaic Structure.*—Any sort of imperfection present in real crystals, with no restrictions as to dimensions, periodicity, or orientation. The term was originally proposed by Darwin in his work on formulas for intensities of X-ray reflection.

*Secondary Structure.*—A term applied to the single, regular (as regards spacing and orientation), submicroscopic structure of crystals proposed by Zwicky.

*Lineage Structure.*—Proposed by Buerger to describe his interpretation of the structure of real crystals, which is, in general: Crystals are partitioned by discontinuities (lineage boundaries) in such a way that the entire structure, descendent from a single nucleus, is continuous but branched.

Metallurgists have done little in the study of mosaic structures, notwithstanding the fact that theoretical metallography must necessarily progress slowly until our knowledge of what constitutes a metallic crystal is much more complete than it is now. The metallographist has been slow in entering the field, possibly because of the fact that the physicist has persisted in relegating the entire phenomenon to a region between 100 and 10,000 Å, and no readily available tool for investigating periodicities of such a magnitude has yet been developed. However, certain indications of a mosaic structure of magnitudes within the visible range are well known in metallography. Among these indications are: (1) translation gliding traces (slip bands); (2) etch figures; (3) the appearance of detail within individual X-ray diffraction spots on photographs of metallic crystals; (4) visible nonuniformity of structure within a single crystal, both in natural and prepared crystals; and so forth.

Mehl<sup>9</sup> has stated that a convincing experimental demonstration defining mosaic structures is necessary before metallurgists as a whole

<sup>8</sup> Reference of footnote 6, 2.

<sup>9</sup> R. F. Mehl: discussion of paper by W. P. Davey, *The Mechanism of Crystal Growth*. *Trans. Amer. Soc. Steel Treat.* (1933) 21, 998-1001.

will adopt the mosaic-structure concept as an important one in the explanation of metallographic phenomena. The writer believes that the following data, procured from the interpretation of detail or fine structure within diffraction spots in unsymmetrical back-reflection Laue photographs<sup>10</sup> of copper single crystals, should tend to demonstrate the importance of the subject.

### PREPARATION OF COPPER SINGLE CRYSTALS

The copper single crystals were prepared by a modification of the Bridgman or Tammann method. The copper used, cathode copper redeposited in pure sulfuric acid, was supplied by S. Skowronski, of the Raritan Copper Works. The cathode pieces as received were cleaned, cut into small pieces, and just before being used were cleaned successively in NaOH solution,  $\text{HNO}_3$ , and KCN solution.

Both Acheson graphite and high-purity transparent silica crucibles were used. The crucible was suspended from a clock mechanism by means of a platinum wire. A platinum-wound verticle tube furnace with automatic temperature control was used; during most of the runs a hot-zone temperature of  $1190^\circ\text{C}$ . was maintained.

Purified and dried nitrogen gas was passed through the tube continuously during the runs. The entire system was gastight except for a small hole at the top of the vertical tube (nitrogen outlet), just large enough to permit free passage of the platinum wire supporting the crucible. After solidification, the crystal was left in the furnace until it had cooled to room temperature. No evidence of oxidation was observed on any of the crystals prepared in this manner.

No difficulty was experienced in the preparation of these crystals; success was 100 per cent. Speeds varying from rapid solidification (no lowering of crystal, but furnace shut off after copper had melted; solidification time about one minute) to a lowering speed of  $1\frac{1}{2}$  in. per 12 hr. were used. Crystals prepared under conditions of rapid solidification showed dendritic structure after a strong electrolytic etch; an example of such structure is shown in Fig. 1. (This crystal was prepared simply by melting the copper in a large graphite crucible in an induction furnace, removing the crucible from the furnace after the copper had reached a temperature of about  $1250^\circ\text{C}$ ., and allowing the covered crucible to cool in air.) Several crystals solidified at a speed of  $4\frac{1}{2}$  in. per hour showed optical mosaic structure similar to that observed by Schilling.<sup>11</sup> Some crystals were sectioned under water with a fine jeweler's saw, and the

<sup>10</sup> A. B. Greninger: Determination of Orientations of Metallic Crystals by Means of Back-reflection Laue Photographs. Page 61, this volume.

<sup>11</sup> H. K. Schilling: Mosaic Crystals of Zinc. *Physics* (1934) 5, 1.



surfaces improved by treatments of successive polishings and etchings, with a final deep electrolytic etch. The majority of the crystals, however, were merely etched in nitric acid, cleaned with KCN solution, and

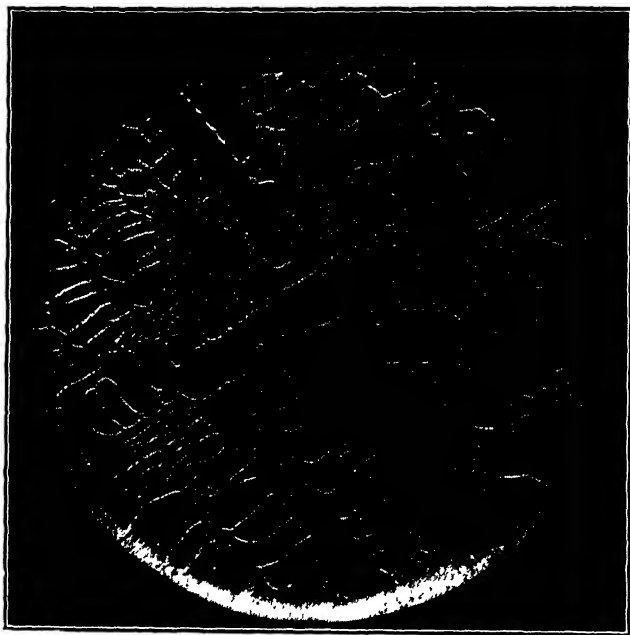


FIG. 1.—SECTION OF RAPIDLY SOLIDIFIED COPPER SINGLE CRYSTAL. STRONG ELECTROLYTIC ETCH.  $\times 7$ .  
For description of crystal see p. 77.

transferred as needed to the goniometer of the X-ray camera. Most crystals were  $\frac{3}{8}$  in. in diameter, and about  $1\frac{1}{2}$  in. long.

#### DETAILS OF X-RAY DIFFRACTION ANALYSIS

The back-reflection Laue method of X-ray analysis previously described by the writer<sup>12</sup> was used. Three different X-ray tubes were used during the course of these experiments; in order, a General Electric tube equipped with a molybdenum target, a Philips-Metalix filament tube with an iron target, and a Müller gas tube with tungsten target. The pinhole system was 1 mm. in diameter, 6 cm. long. Excitation potentials varied from 30 to 35 kv. (r.m.s.). The crystal-to-film distance was 3 cm. An Eastman "super" intensifying screen was used. Exposure times varied, according to the X-ray tube used, from about 36 hr. for the General Electric diffraction apparatus to about 3 hr. for the Müller gas tube equipped with tungsten target.

<sup>12</sup> Reference of footnote 10, 3.

The crystals were supported on the goniometer of the X-ray camera either by means of picene on a flat disk or by a special cylindrical crystal holder in which the crystal was held by light friction in contact with lens paper.

Photographs were taken at various points on both the surfaces and interiors (etched) of the crystals. Most of the photographs, however, were taken in the region near the nucleus.

## RESULTS

Of the fifty-odd photographs obtained, none failed to show fine structure in at least a few of the Laue spots, although not all of the photographs contained spot detail sufficiently sharp to permit interpretation.

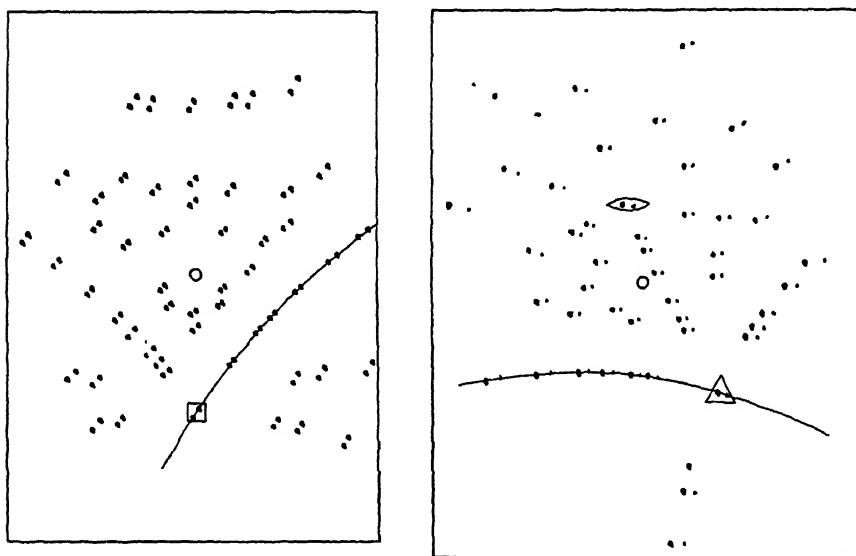


FIG. 2.—TRACINGS OF BACK-REFLECTION LAUE PHOTOGRAPHS OF TWO COPPER SINGLE CRYSTALS, SHOWING WELL DEFINED LINEAGE STRUCTURE.

□ = {100}, Δ = {111}, ○ = {101}. Common [101] directions indicated by hyperbolic curves. In original photographs, some spots showed evidence of "sub-lineage" structure.

In several photographs uniform sharp detail was obtained in all spots. This detail in spots is evidently caused by the X-ray beam's striking two or more major lineages which differ by a measurable small degree from exact parallel orientation. The appearance of detail in some spots and not in others on the same photographs is due largely to the variable penetrating power of the different wave lengths that take part in the diffraction. The ideal photograph for interpretation is obtained when the X-ray beam strikes only two or three major lineages to adequate depth, so that diffraction is effectively confined to them alone.

Fifteen of the photographs taken to date contained fine structure sufficiently defined to permit interpretation. Lineages deviate from exact parallelism from as little as 5 or 10 min. to as much as  $2^\circ$ . A few photographs contained sharp detail of more than two lineages; others exhibited definite sublineage structure. (See page 82 for discussion of this structure.)

### *The Common Direction—[uvw]*

The common direction of any two neighboring lineages was relatively easy to determine. If two neighboring lineages, differing slightly in orientation, have a common zone axis, the resulting pertinent Laue spots will line up along the corresponding hyperbolic zonal curve on the back-reflection Laue pattern. That is, two lineages having a common zonal curve on the Laue pattern must have a common crystallographic zone axis in the crystal. When coincidence is judged, allowance must be made for the width of the X-ray beam (1 mm.).

Several good photographs were obtained, inspection of which led to the conclusion that neighboring lineages have a [110] or a [100] direction in common. The [110] direction predominates. The score of all photographs examined was as follows:

Well defined common [110] direction.... .	6
Possible common [110] direction... .	1
Well defined common [100] direction. . . .	1
Possible common [100] direction .. . .	2

Tracings of two of these photographs are reproduced in Fig. 2.

### *Interlineage Boundary Plane—{hkl}*

After the existence of a common direction of neighboring lineages had been discovered, it was evident that such uniformity of structure building, predominantly centered on crystallographic directions of closest atomic approach, pointed to the possibility of a definite type plane, or at least of a predominating type plane, of contact between lineages. The common direction of two lineages is probably not as important structurally as would be the contact plane or "interlineage boundary plane."

The contact-plane concept may be clarified by considering Fig. 3. In this figure, the orientation of the original nucleus is represented by cube A. The two lineages, differing slightly from parallelism and having a common [110] direction ( $xy$ ), are represented as cube segments  $A_1$  and  $A_2$ . With no additional crystallographic definition of lineages  $A_1$  and  $A_2$ , the boundary plane could be any crystallographic plane. However, knowing the great importance in crystal behavior of lattice planes of lowest indices, one might expect this "plane of contact" to be such a

lattice plane. Further conjecture might lead one to select as most favored the  $\{111\}$  type plane, inasmuch as it is the plane of most dense packing of atoms in a face-centered cubic lattice, the most widely spaced plane, and also has the largest number of  $[110]$  directions.

The trace of a contact plane on the crystal surface should be projected on to the photographic film when the following conditions are fulfilled: (1) The X-ray beam must strike a lineage boundary that approximates a straight line for a distance of  $\frac{1}{4}$  mm. or more; (2) the two neighboring lineages must contain no mosaic structure that would prohibit the sharp projection of the contact-plane trace; (3) the lineages must differ in orientation by not more than  $\frac{1}{2}$  or  $\frac{3}{4}$  degree, preferably by not more than 5 or 10 min.; (4) the exposure of the photographic plate must not be such that the trace-projection is obliterated by overexposure. With these conditions fulfilled, at least a few of the resulting Laue spots should be resolved into two or more adjacent spots separated by a "line" devoid of blackening; this "line" should be a projection of the trace of the interlineage boundary plane.

Also, one or more boundary-plane traces may be projected on to the photographic film as a small blackened line or lines<sup>13</sup> within individual Laue spots; i.e., the intensity of blackening of the line will be greater than that of the rest of the Laue spot. This results when a narrow lineage has a higher maximum reflecting power than the other lineages that the X-ray beam strikes.

These conditions were fulfilled in a few of the photographs obtained. Traces of principal isometric forms were located on stereographic projections of each of the suitable photographs, and each photograph was then superimposed upon its corresponding stereographic projection. In all these photographs except two the projection of the traces on the film correspond with the stereographic projection of a  $\{111\}$  trace. The definite exceptions were those in which the projection of the trace on the film corresponded with a  $\{100\}$  or  $\{110\}$  trace. Because of the near symmetry of the Laue patterns, the pertinent  $\{100\}$  and  $\{110\}$  traces could not be differentiated. The score of all photographs interpreted was as follows:

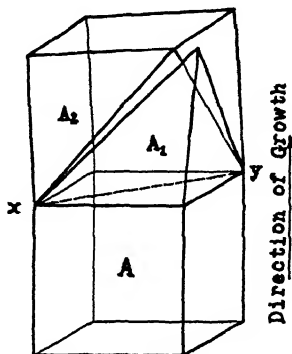


FIG. 3.—SIMPLIFIED AND EXAGGERATED DIAGRAMMATIC REPRESENTATION OF CRYSTALLOGRAPHIC RELATIONS BETWEEN NUCLEUS AND FIRST TWO LINEAGES OF A CUBIC CRYSTAL.

As represented, common direction is  $[110]$ , contact plane is  $\{111\}$ . Only one direction of growth assumed.

<sup>13</sup> This phenomenon ("ghost lines") is a well known source of possible error in X-ray spectroscopy.

Well defined {111} trace-coincidence . . .	9
Possible {111} trace-coincidence . . . . .	3
Well defined {100} or {110} trace-coincidence . . .	2
Possible {100} or {110} trace-coincidence . . . . .	1

### DISCUSSION OF RESULTS

The experimental results are obviously not conclusive proof that a definite interlineage type plane exists. However, the evidence in support of a simple crystallographic zone-axis relation seems adequate. The method can give greater resolution, and consequently greater accuracy, when used for determining direction relations. The traces of contact planes that appear on the photographs are not more than 1 or 2 mm. long, and an error of 2° to 5° may easily be made in prolonging the traces.

Knowing the simple direction relation, perhaps we are warranted in assuming that if a predominating interlineage contact plane existed it would be one of the three important planes of the face-centered cubic lattice. Our assumption would be unjustified if the results had shown a more or less equal distribution of near trace-coincidences among the {111}, {110} and {100} planes. The many cases in which the projection of the trace of the supposed plane of divergence corresponded with {111} traces, as well as the shortcomings of each individual trace-coincidence as proof of a plane-coincidence, should be considered in judging the value of the data.

The picture of lineage structure, even as regards single copper crystals grown from the liquid phase, is admittedly incomplete. A description of this lineage structure, which may be made tentatively from the data available at present, is as follows: Copper single crystals as a whole possess a network of mosaic structure predominantly delineating the {111} planes, with any two neighboring lineages having a [110] direction in common; a less frequent uniformity is a delineation of {110} or {100} planes with common [100] direction. Observations have been made only on the lineage structure that may be defined as macroscopic or large-scale. These major lineages unquestionably are subdivided by a finer network of lineage structure. A number of photographs demonstrate the crystallographic uniformity of the sublineage structure large enough to be resolved by X-rays; therefore, it is probable that all lineage structure, down to the smallest imperfections, has a like uniformity. The sizes of these major lineages and their angular deviation vary considerably, even for adjacent regions of the same copper crystal. No statement can be made at present concerning the degree to which these variations depend upon growth conditions; work on this point is in progress.

According to the foregoing picture, a {111} plane of a copper single crystal is not one uniform surface but consists of a large number of major interlineage boundary planes (macroscopic) differing slightly in

orientation; and these major interlineage planes in turn are made up of many smaller planes inclined at slight angles to one another. Therefore all of the (111) parallel crystal planes (or any other set of parallel crystal planes) are not structurally or crystallographically identical; some will be more nearly perfect than others.

The concept of a crystallographically uniform lineage structure might help to explain many puzzling phenomena observed in metals and alloys. However, too little is known about the subject at present to warrant theoretical comparisons, other than the observation that the predominating lineage relations coincide with the translation gliding elements of copper,  $T = \{111\}$ ,  $t = [110]$ .

### CONCLUSIONS

The interpretation of fine structure within individual spots on unsymmetrical back-reflection Laue photographs of copper single crystals indicates that such crystals possess a crystallographically uniform lineage structure.

Predominant relation between neighboring lineages is:

Common direction  $[110]$   
Interlineage boundary plane  $\{111\}$

Less frequent relation is:

Common direction  $[100]$   
Interlineage boundary plane  $\{110\}$  or  $\{100\}$ .

### ACKNOWLEDGMENT

Thanks are tendered to Dean H. E. Clifford and the Harvard Engineering School for the facilities and aid that are making this research possible. For many fruitful discussions the writer is greatly indebted to Prof. M. J. Buerger, of Massachusetts Institute of Technology, whose attractive theory of lineage structure prompted this research. Professor Buerger and Prof. J. T. Norton read the manuscript and examined the photographs.

### DISCUSSION

*(Eric R. Jette presiding)*

G. E. DOAN,\* Bethlehem, Pa.—I should like to ask Mr. Greninger whether he does not believe the structure that he shows in Fig. 1 to be that of copper dendrites in a copper-copper oxide eutectic. If I had cooled a melt of pure copper from  $1250^{\circ}\text{C}$ ., even in a covered crucible, and obtained such a structure, I should suppose it to be the alloy just mentioned. Copper at these temperatures takes up oxygen rapidly.

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\* Associate Professor of Metallurgy, Lehigh University.

R. F. MILLER,\* New Haven, Conn. (written discussion).—Evidence of the crystallographic uniformity of the lineage structure in zinc single crystals was noted by Dr. Buerger in his article on the Lineage Structure of Crystals.<sup>14</sup> The zinc dendrites of the fir-tree type shown in Fig. 1 of his article were found to have their main trunk parallel with the  $c$  axis, with the boughs or side-arm lineages running in the direction of the  $a$  axes. They are typical of dendritic crystals grown freely from a vapor or a melt, where the material is added to the nucleus from all sides. The direction of slowest growth (the direction of the trunk lineage) is normal to the plane of densest atomic packing.

However, in the Bridgman method, growth proceeds in only one direction from a nucleus. The crystal-liquid interface is approximately normal to the direction of growth, and reaching out from it are many parallel, uniformly spaced dendrite fingers. Whether they are main or side-arm dendrites is determined by the orientation of the nucleus relative to the direction of growth. In zinc crystals, if the (0001) plane is about normal to the direction of growth, the trunk ( $c$  axis) lineages will develop. If the (0001) plane is about parallel with the direction of growth, the side-arm lineages will build out in one of the  $a$ -axis directions. If the (0001) plane is oblique, both may develop, as shown in Fig. 4. The direction from which the new material is being added also seems to influence the dendrite directions, making them more nearly parallel with the direction of growth. Dr. Buerger called attention to the fact that the outline of the trunk lineage was hexagonaloid, while the cross section of the  $a$ -axis lineages had twofold symmetry.

The crystallographic uniformity of these zinc lineages is also shown by Fig. 5 of the same article. In the upper left-hand corner there remains a fragment of the overlying basal plane. The cleavage edge shows the direction of an  $a$  axis. If lines are drawn across this picture parallel with this  $a$ -axis direction, the lineages, assuming that their length is normal to the plane, have prism (10 $\bar{1}$ 0) faces as their planes of contact. These lineages also have common directions, such as [0001] and [11 $\bar{2}$ 0].

I should like to ask Mr. Greninger whether his specimens of copper crystals that showed a common [110] direction in neighboring lineages were the same ones in which (111) was found to be the interlineage boundary plane, and whether the crystal showing the common [100] direction of the lineages had (110) as the interlineage boundary plane; these are the relationships that might be predicted from the theory of the growth of crystals.

In a freely growing copper crystal, it would be expected that the major "trunk" lineages would be normal to the close-packed (111) planes, and that each trunk lineage would be accompanied by sub-lineages or "boughs" extending out at right angles in the [110] directions. Imagining a tetrahedron as the nucleus in a Bridgman specimen of copper, at most only one trunk lineage direction is possible; the others point to the bottom or bottom sides of the mold. If a transverse position of the (111) plane should occur, "trunk" lineages would develop in the [111] direction. The planes of contact between the lineages would also be normal to the (111) plane; they could be dodecahedral (110), but not (100), since the cube plane is not normal to the (111) plane. Mr. Greninger's X-ray evidence shows that either (110) or (100) is possible, but consideration of the growth mechanism makes it seem likely that (110) is the correct plane. In this "less frequent" group, the [100] direction is indicated as common, whereas the [111] direction might have been expected. However, this is verified by only one specimen, which may not have been the one to show (110) as the interlineage boundary plane.

\* Graduate School, Yale University.

<sup>14</sup> Reference of footnote 6.

If the tetrahedral face should occur oblique to the direction of growth, as is more likely to happen, the side-arm lineages would predominate. These would follow a [110] direction (direction of greatest linear atomic density). The planes of contact would be the (111) planes, with [110] as the common direction. This is the "predominant" lineage relationship given by Mr. Greninger. That this should be the case most frequently encountered is also understandable, since there are six possible sub-lineage directions (either way on the three [110] directions), while there is only one possible trunk lineage direction (normal to the one tetrahedral face which could be transverse to the direction of growth).

The possibility that the lineages appearing in a Bridgman crystal of copper may be either main or side-arm lineages, depending on the direction of growth from the randomly oriented nucleus, accounts for the discovery by Mr. Greninger of two groups of orientation relationships, one of which appears oftener than the other. It would be of much interest to know whether the majority of Mr. Greninger's crystals were so oriented relative to the direction of growth that the side-arm lineages had a better chance of developing than did the main trunk lineages.

H. H. LESTER,\* Watertown, Mass. (written discussion).—In view of observations extending back perhaps to 1905, there can be little question of the existence of irregularities in crystal structures. There has been needed a clearly presented picture of the phenomena called mosaic or lineage structures for the benefit of those who are interested primarily in metals. There is needed, also, a clear exposition of the causes of such imperfections and an interpretation of their effects in terms of physical properties of crystalline materials.

At first sight, one might infer that lineages might serve merely to further granulate an already granulated material, and, as such, make for grain refinement in polycrystalline materials, such as steel. However, it has been shown that the actual strength of a carefully prepared single crystal falls far short of its theoretical value, at least for the materials of interest to industry.

It would appear, therefore, that individual crystallites in a multiple-grained material do not reach their theoretical strength. Whether or not greater knowledge would lead to improved strength of individual grains and hence of the crystalline mass, is a question that can be answered only after the accumulation of data that may require years of study.

Because of this direct connection, Mr. Greninger's study is of great importance to physical metallurgy. His attack shows an appreciation of the desirability of presenting a concept of the irregularities in clearly defined terms, a necessary beginning point in the understanding of them. He has selected copper as a material for study, perhaps because it has a relatively simple lattice and can be obtained in a state of high purity, and wisely confines his study to facts of occurrence rather than to causes. It is to be hoped that later efforts will aim at elucidation of causes, effects on physical properties, and possible methods of control.

It is to be noted that this paper seems to present the first fruits of the new method of X-ray analysis recently developed by Mr. Greninger.

G. EDMUNDS,† Palmerton, Pa.—Dr. Wheeler P. Davey has asked me to present discussion in his absence, as he had to return to State College. The remarks will be an attempt to give you the information he has asked me to present, and will in no way be my feelings in regard to the subject.

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\* Research Physicist, Watertown Arsenal.

† Research Laboratory, New Jersey Zinc Co.



About 10 years ago, Dr. Davey, in working with copper crystals that were grown in a horizontal furnace by the Bridgman method, obtained some large crystals from busbar copper. During the growth of one of these, he removed a growing crystal from the furnace and at once inverted it so as to throw away from the solidifying single crystal the liquid metal that was adjacent to it.

Fig. 4 shows a cross section taken through the region from which the molten metal was thrown out. Part A represents an area that was freezing at the time, and the other parts show the shaper marks where the single crystal was sectioned.



FIG. 4.

He then took a photomicrograph (Fig. 5) of the hole A at a somewhat higher magnification. In this the small needles are shown to a certain extent, and extend out in various directions toward the molten mass. The shaper marks that appeared on the natural size photograph are also included in Fig. 5. Under better conditions of observation, according to Dr. Davey, the form of the needles was definite, and he therefore presents this as evidence of a lineage growth of a single crystal.

He assumes that lineage growth takes place as if from the intersections of discontinuities in a crystal. In other words, the intersection of these discontinuities gives rise to either four small lineages, as illustrated in Fig. 6 (A) coming outward from the plane of the paper, or one, Fig. 6 (B), in either case the two different possibilities being indistinguishable because of their small size.

As to whether or not the lineages themselves, are discontinuous, Dr. Davey has furnished Fig. 7. This shows the polished section of a copper single crystal grown by the Bridgman method. In this are shown what appear to him to be lineage growths, with the plane of polish almost parallel to the lineages. This approximate parallelism is evidenced by the lineages being wider on one side and apparently narrowing on the other, due to going either below or above the surface.



FIG. 5.

The secondary lineages which have filled in between the primary ones are also shown, and, according to Dr. Davey's theory (Fig. 6), these secondary lineages must have arisen from discontinuities in the original ones. He therefore postulates that these original lineages are not continuous, but rather discontinuous, and therefore give rise to the secondary lineages by the same mechanism as that of the primary ones.

A. B. GRENINGER (written discussion).—Professor Doan's question regarding the structure shown in Fig. 1 cannot be answered directly. The structure does resemble that of a copper-copper oxide eutectic on a large scale. Photomicrographs of several areas of the same specimen failed to reveal any evidence of "small-scale" eutectic. Furthermore, dendritic structure was also found in copper crystals prepared at relatively high solidification speeds in an atmosphere of purified nitrogen.

It is certainly true that dendritic structure of a metal is revealed by etching only because of the presence of chemical or physical heterogeneity. Attempts to differentiate between these, or to select one element that may be responsible for the etching effect, usually can be nothing more than conjecture.

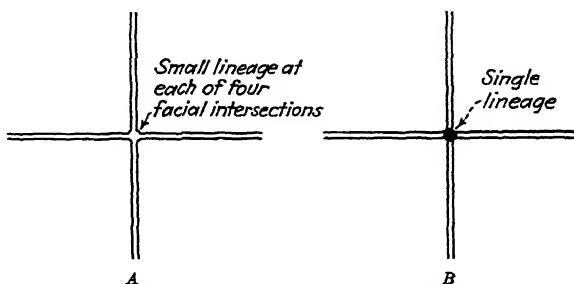


FIG. 6.—*A*, FOUR LINEAGES (EXTENDING OUTWARD FROM PLANE OF PAPER) DEVELOPED AT INTERSECTION OF DISCONTINUITIES OF CRYSTAL; *B*, SINGLE LINEAGE (COMING OUTWARD FROM PLANE OF PAPER) DEVELOPED AT INTERSECTION OF DISCONTINUITIES OF CRYSTAL.

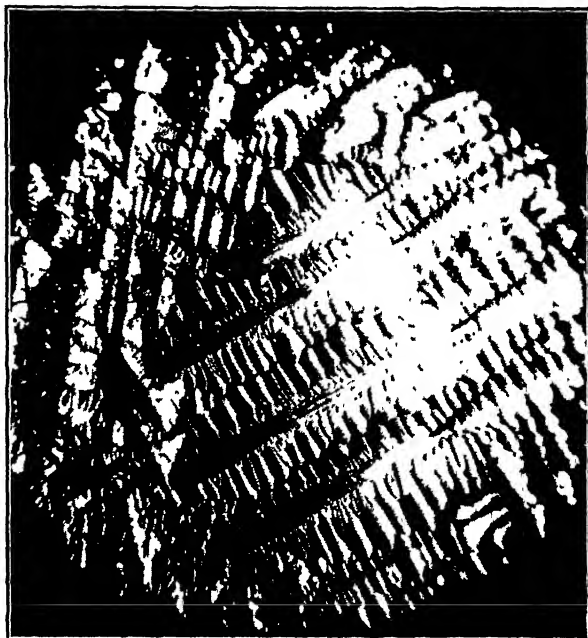


FIG. 7.

In answer to Dr. Miller's first question: The X-ray method used did not permit a determination of both common direction and interlineage boundary plane on the same lineage. However, in two cases in which lineage boundary plane traces could be determined by optical methods there was no absolute uniformity such as that suggested by Dr. Miller. In one case, in which the common direction was  $[100]$ , the traces found were  $\{100\}$  and  $\{110\}$ .

Unfortunately, some misunderstanding has arisen because the author used the term "lineage structure" to designate large-scale mosaic structure, while Professor Buerger originally used it in his discussion of zinc crystals as indicative of, but not restricted to, the more familiar dendritic structure.

Conclusions stated in this paper do not apply to dendritic structure, but to individual mosaic blocks, which often show an elongated habit, undoubtedly due to columnar growth. In a future publication the writer will attempt to give a more complete description of this structure which gives rise to splitting of spots on back-reflection Laue patterns.

## Influence of Lattice Distortion on Diffusion in Metals\*

BY VICTOR G. MOORADIAN† AND JOHN T. NORTON,‡ MEMBER A.I.M.E.

(Chicago Meeting, October, 1935)

THE diffusion of metal atoms into the crystal lattice of another metal and the assumption of regular positions to form a homogeneous alloy are some of the most fundamental phenomena of structural metallurgy. The mechanism of this process has been the subject of a great deal of study from many viewpoints, but the picture is still far from complete. It is generally believed that if one metal is to diffuse into another, the first must have some solubility in the second<sup>1</sup>. This means that the solvent must be able to accommodate the stranger atoms, either on points of its own lattice or in the interstices between, without losing its own crystallographic identity. It is also a general observation that cold-working is a distinct aid in the diffusion process, causing it to take place with greater rapidity at the same temperature or with the same speed at a lower temperature. There is considerable doubt, however, as to the real significance of the deformation in its effect on the diffusion mechanism.

Several factors associated with the cold-working may be responsible for the increased diffusion rate. The plastic deformation causes a distortion of the solvent lattice, which may be an aid in the assimilation of atoms of another kind. There are many references<sup>2</sup> in the literature that suggest that some distortion or "loosening" of the lattice is necessary for atomic migration and that diffusion cannot take place in the undistorted lattice. On the other hand, it may be that the cold-working causes an increase in surface of contact between the two metals through fragmentation or provides a more intimate contact that is necessary for diffusion. If it is true that lattice distortion is an important factor in diffusion, it seems as if there should be some particular relation between

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\* These experiments represent a portion of a thesis presented by V. G. Mooradian in fulfilling the requirements for the degree of Master of Science at Massachusetts Institute of Technology. Manuscript received at the office of the Institute June 17, 1935.

† Assistant Instructor, Department of X-ray Metallography, Graduate School of Engineering, Harvard University, Cambridge, Mass.

‡ Associate Professor, Department of Mining and Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.

<sup>1</sup> Desch: Chemistry of Solids, 111. 1934.

<sup>2</sup> Desch: Reference of footnote 1, 110-111.

the temperature of recovery from deformation and the temperature necessary to cause diffusion. A demonstration that recovery takes place before diffusion begins would be a strong argument against the idea that lattice distortion aids the diffusion process. On the other hand, if the migration of atoms takes place in the distorted lattice more easily than in an undistorted lattice, it suggests that the distortion really plays some part.

The following experiments were undertaken to test this point. They cannot be considered as critical because of the limited number of systems examined and the results are essentially qualitative, but they supply some interesting results and suggest possibilities for further work.

### EXPERIMENTAL PROCEDURE

In the present experiments, diffusion was produced by heating a duplex sample of the two metals in question to a series of different temperatures. Four different binary systems were examined: copper-nickel, copper-gold, silver-gold and nickel-cobalt. These all form continuous series of solid solutions. The duplex sample was made by electrodepositing thin layers of the two metals alternately on top of one another to form a thin sheet. The relative amounts of the two metals were regulated so that X-ray diffraction lines of approximately equal intensity were obtained. The electrolytic method was chosen because the metals could be obtained quite pure, in intimate contact and with a certain amount of lattice distortion. The individual layers were so thin that the X-ray diffraction patterns were truly representative of the interior of the sample.

The samples were heat-treated in evacuated tubes of Pyrex glass. The heating was carried out at successively higher temperatures. At the end of 24 hr. at each temperature, the sample was removed, examined and returned to the furnace for the next higher temperature. The 24-hr. period was chosen arbitrarily for these particular experiments.

The principal observations of these specimens were made by the X-ray diffraction method. The X-ray line width and line position are excellent indications of the condition of the sample during the various stages of diffusion. The Phragmén type<sup>3</sup> of X-ray camera was employed and the electrodeposited flat sheet was mounted on a slip of paper, which permitted it to conform to the curve of the camera. The experimental set-up is shown in Fig. 1. This arrangement gives a considerable number of lines as well as good resolution of the lines themselves and is well suited to a problem of this type. During the work the details of the experimental set-up were kept constant so that any changes in line

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<sup>3</sup> Westgren: *Trans. A.I.M.E.* (1931) 93, 13.

width are due to variations in the sample. A suitable sample free from strain gives sharp, clear lines with a good separation of the  $K$  alpha doublet at the larger angles.

The appearance of a wide line in the X-ray photogram may be indicative of any of three situations in this particular case; namely: fine grain size, lattice distortion, and variable composition from point to point. In the original electrodeposits, the width of the lines is probably due to lattice distortion. Such deposits are known to be under considerable mechanical strain and there is no evidence of the presence of an extremely fine grain structure. Certainly there is no variation in composition. On the other hand, if diffusion of the adjacent layers begins, the X-ray lines will change in position, indicating a change in composition, and if at the same time they become wide, this shows that the composition is not uniform throughout. Sharp lines indicate a uniform homogeneous structure, free from strains. These features make the X-ray method particularly useful in this problem.

The X-ray method of studying the diffusion process is, of course, based upon the formation of a solid solution with its consequent change in lattice parameter. This assumes that when atoms of one kind diffuse into a lattice of another kind, a true alloy is formed, and there is every reason to believe that this assumption is correct. In order to avoid confusing effects, systems were chosen that were completely soluble in one another. The position has been taken that the formation of a solid solution implies diffusion, and conversely that no formation of solid solution means that diffusion has not taken place. It is believed that this stand is fully justified.

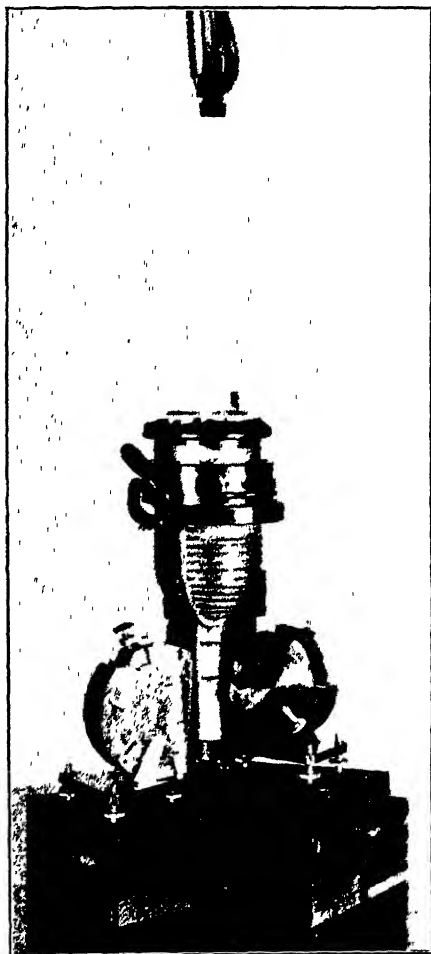


FIG. 1.—SIEGBAHN-HADDING X-RAY TUBE AND PHRAGMÉN CAMERAS FOR EXAMINATION OF ELECTRODEPOSITS.

## EXPERIMENTAL RESULTS

The experimental observations on the four systems investigated are in complete agreement and can be described in a simple manner. The original deposits all show rather broad lines. The electrodeposited

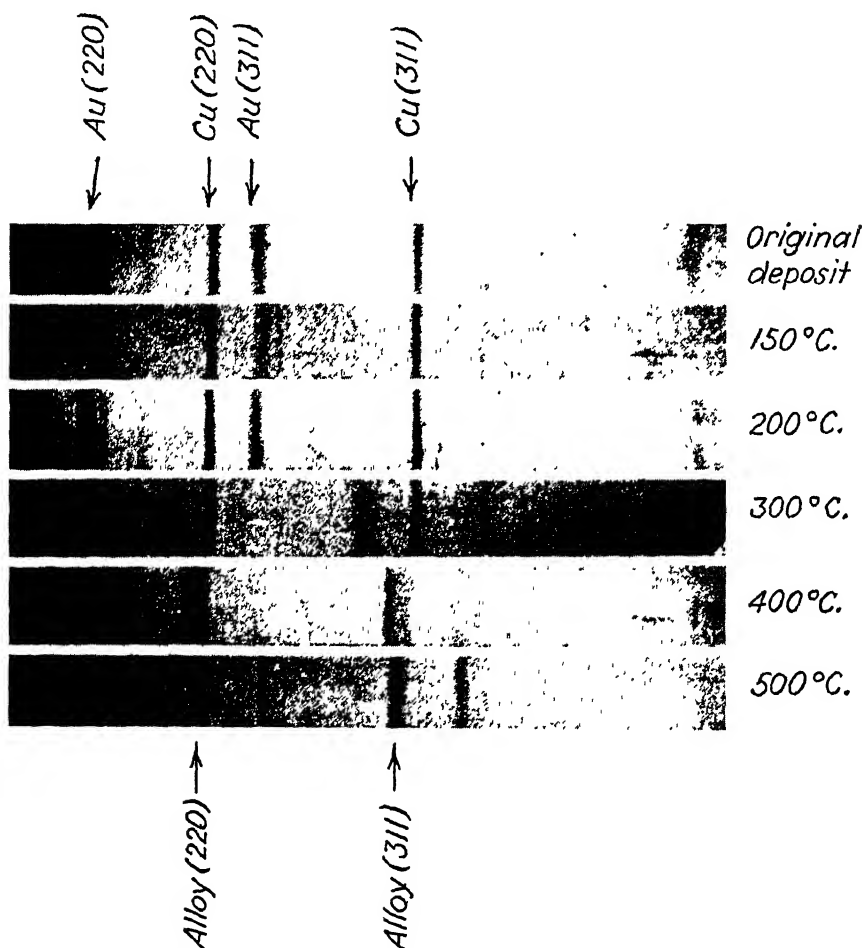


FIG. 2.—COPPER-GOLD SYSTEM. TAKEN ON CAMERA OF INTERMEDIATE RANGE WITH COPPER RADIATION.

copper shows less distortion than the other metals but upon heating for 24 hr. at temperatures as low as 150° C., the lines in all the samples become sharper. After passing through a sharp stage, further heating causes the lines to move to new positions and again become broad. Higher temperature causes the lines of the two metals to merge into a single set of broad lines, which again sharpen up at still higher temper-

atures. Fig. 2 shows the situation in the copper-gold system. The photograms were taken on a camera of low dispersion, so that the  $K$  alpha doublet is never clearly resolved; but it presents a general view of the situation. Both sets of lines are broad in the original deposit, the gold more so than the copper. At 150° C. there is some improvement in

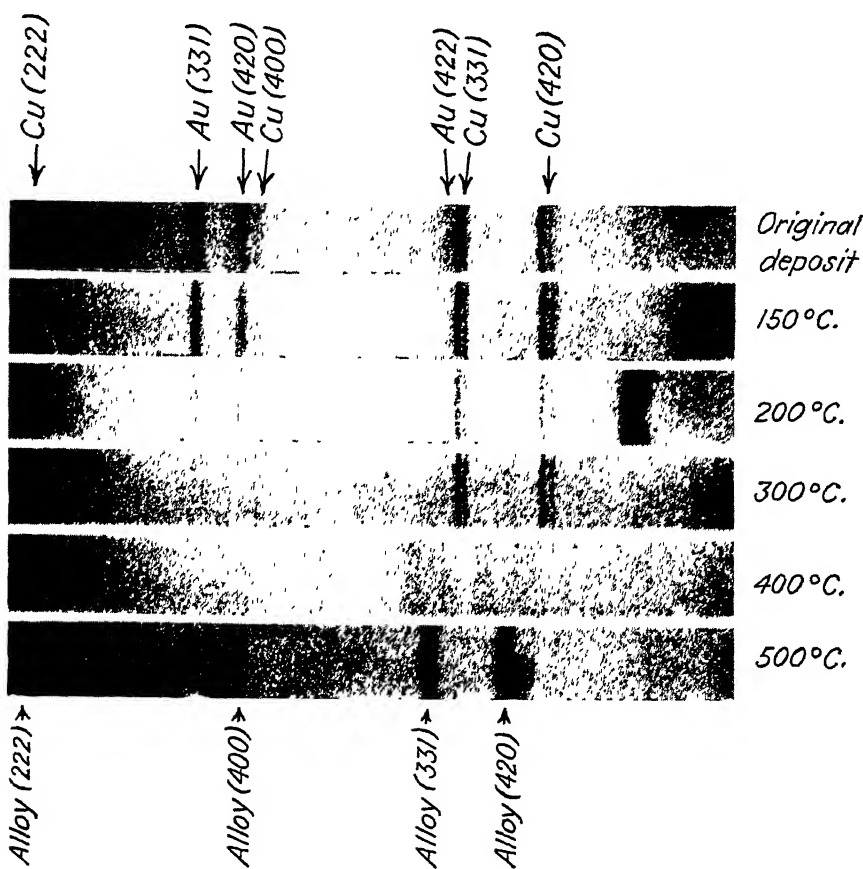


FIG. 3—COPPER-GOLD SYSTEM. SAME SAMPLES AS FIG. 2 BUT TAKEN ON CAMERA GIVING LARGE DIFFRACTION ANGLES. COPPER RADIATION.

sharpness, and at 200° C. still more. There is no change in line position up to this point. At 300° C., however, a real change has taken place. On one hand, the gold lines have moved decidedly toward the corresponding copper lines and have become quite broad. On the other hand, the copper lines have not moved at all and have become even sharper. Thus the recovery temperature of the gold is somewhat above 200° C., while that of copper is above 300° C. The copper has begun to be dissolved by the gold at 300° C. but at this temperature none of the



gold has been dissolved by the copper. At 400° C. mutual solubility has begun and a broad line of the alloy only is visible. The original

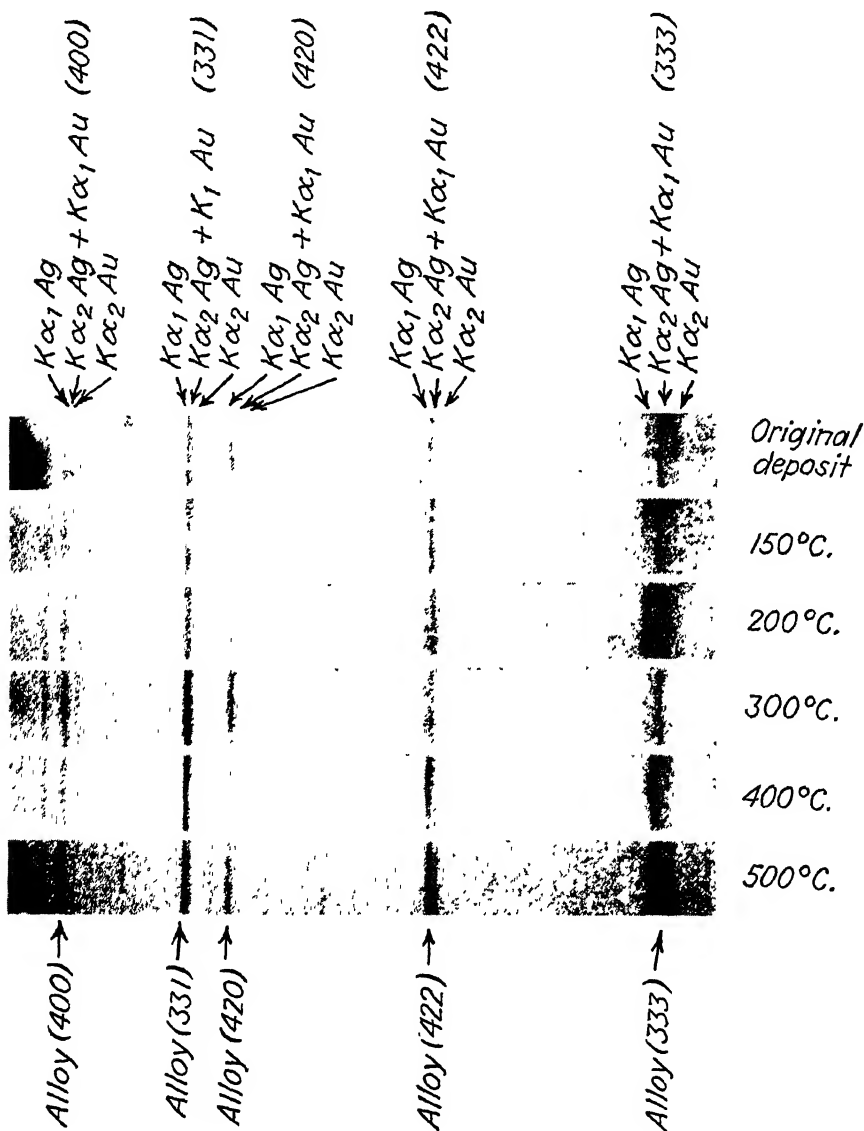


FIG. 4.—SILVER-GOLD SYSTEM. CAMERA GIVING LARGE DIFFRACTION ANGLES. COPPER RADIATION.

copper lines have disappeared. It is not clear why the alloy lines are doubled but it suggests that there are two regions of the specimen of different composition. At 500° C. reasonably sharp lines of the homogeneous alloy are seen.

The same steps can be followed in the photograms of Fig. 3. These are of the same samples but taken on a camera that records the higher diffraction angles. Again the lines of both metals become sharper up to 200° C., but there is no diffusion. At 300° C., the gold lines have moved and become so diffuse that they are scarcely visible in the reproduction of the photograms, but the copper lines have become sharper without change in position. A temperature higher than 500° C. would be required to completely homogenize the final alloy.

Fig. 4 shows a similar set of photograms for the silver-gold system. In this, the parameters of the two metals are so nearly the same that the  $K\alpha$ -1 line of gold falls on top of the  $K\alpha$ -2 line of silver and the result appears as a triple line. As deposited, the lines are slightly broadened although the doublet separation is clearly seen. At 150° and 200° C. there is a sharpening of the lines, indicating recovery, the maximum sharpness being reached somewhat above 200° C. At 300° C. a slight broadening is observed, indicating the beginnings of diffusion. At 400° C. definite diffusion has taken place and the triple line has become a rather broad doublet. The alloy has become completely homogeneous at 500° C., as shown by the single set of sharp clear lines. These changes can be followed very definitely from the photo-densitometer records of these same photograms shown in Fig. 5. The changes in the sharpness of the lines and the formation of the alloy can be clearly seen.

The copper-nickel alloys show exactly the same mutual diffusion as described above, and the cobalt-nickel give indications for a similar behavior, although the presence of a considerable amount of the hexagonal cobalt complicates the situation.

#### DISCUSSION OF RESULTS

The experimental results described are rather limited in scope and no very broad conclusions can be based upon them without further work, but certain features are worthy of discussion. The results show definitely that the lattice distortion in the original samples is not an aid to diffusion, because it disappears in every case before diffusion starts. Furthermore, it may be a distinct hindrance and its removal a necessary factor before easy diffusion can take place.

The experiments also show that the diffusion of two metals in intimate contact may not be mutual. In the copper-gold alloys, copper has diffused into the gold at a lower temperature than gold into copper. Is this due to the fact that gold recovers at a lower temperature than the copper and thus makes easy diffusion possible, or merely that the small copper atoms diffuse more readily than the larger gold atoms? The results are not sufficient to answer this. It does show, however, that silver and gold, which are of the same atomic radius, diffuse mutually, and the same is true of copper and nickel, which are of nearly the same size.

But in these two systems, the recovery temperatures of the pairs are also closely alike. This point must be the subject of further investigation.

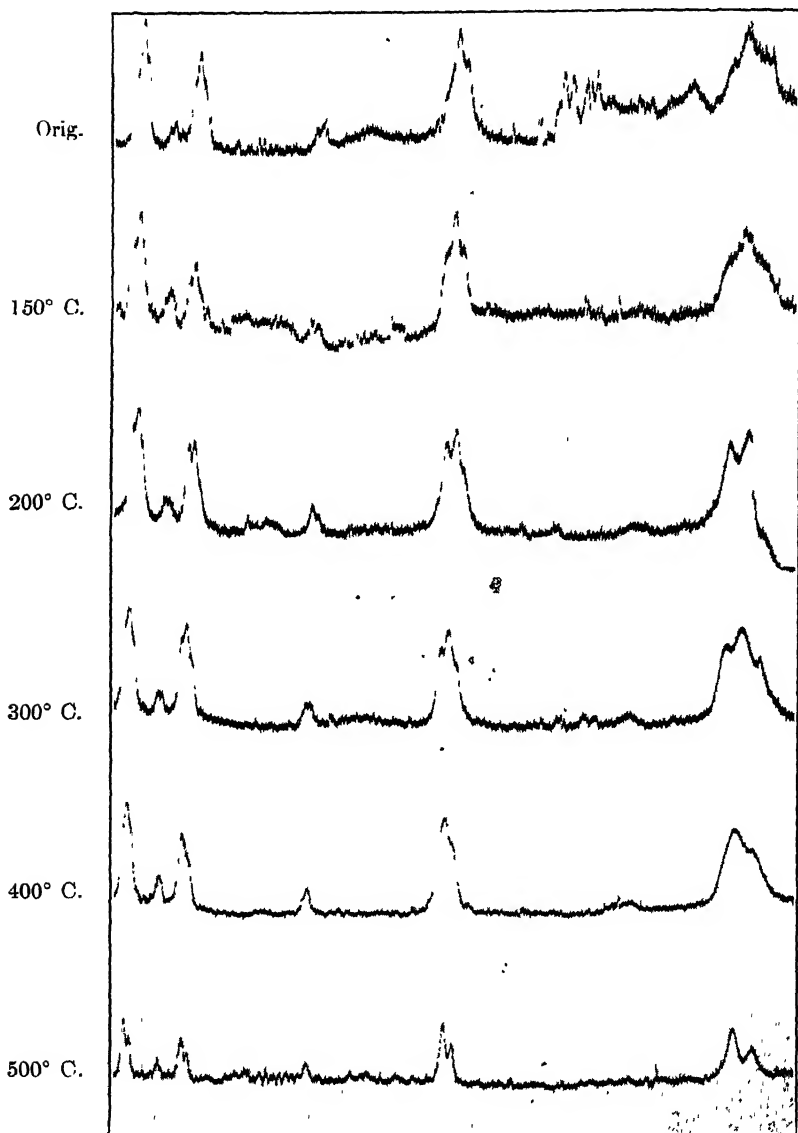


FIG. 5.—PHOTO-DENSITOMETER RECORDS OF PHOTOGRAMS OF FIG. 4.

One might ask whether the recovery temperature would not always be lower than that of easy diffusion. Recovery is believed to be the return of atoms of the distorted lattice to their normal positions under the influence of the lattice forces and increased thermal vibration, a

movement generally less than the interatomic distances. Diffusion, on the other hand, involves very large atomic movements and consequently requires greater thermal agitation. Unfortunately, too little is known about the process by which an atom moves through the lattice. Undoubtedly some sort of discontinuity is required, which may take the form of the "dislocation" described by Taylor<sup>4</sup> and the atoms may pass from point to point in this way. This type of dislocation is not equivalent to the general lattice distortion that causes line broadening. Perhaps, then, the relative temperatures of recovery and diffusion represent merely the natural sequence of events during heating and are not directly connected with one another. But the main conclusion is that lattice distortion is not necessary to diffusion.

As far as the authors are aware, no direct observations of the influence of general lattice distortion on diffusion have been made previously and it is hoped that these preliminary results will stimulate further investigation in this important field.

#### ACKNOWLEDGMENTS

The authors wish to acknowledge the use of the facilities of the X-ray metallography laboratory at Massachusetts Institute of Technology, and are indebted to Dr. H. H. Lester, of the Watertown Arsenal, for the use of the photodensitometer.

#### DISCUSSION

(*Samuel L. Hoyt presiding*)

R. F. MEHL\* AND C. S. BARRETT,\* Pittsburgh, Pa. (written discussion).—There are few subjects of more importance in the science of metals than that of diffusion in solid metals, yet there is much confusion in the field and a very great deal of rather simple experimentation remains to be done. This paper, the first to appear before this society since Dr. Hoyt<sup>5</sup> reported on diffusion of zinc in brass and Mr. Kelley<sup>6</sup> reported on diffusion in coated metals, strikes at one of the troublesome features of diffusion; namely, the effect of distortion on the rate of diffusion. Stated briefly, Mr. Mooradian and Dr. Norton have shown that an electrodeposit is rendered free from strain and from abnormally fine grains by a heat-treatment insufficient to cause a measurable diffusion. The importance of this subject would seem to warrant a rather careful discussion.

The discussion of distortion and "lattice loosening" in relation to diffusion has come chiefly from two sources, one theoretical and one experimental. The dependence of the diffusion coefficient upon temperature may be represented by an exponential function, in the exponent of which is placed an energy term by analogy with the heat of activation term in the function representing the rate of chemical reaction in dependence upon temperature. This energy term, the "heat of diffusion," has been identified

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<sup>4</sup> Taylor: *Proc. Roy. Soc.* (1934) **A145**, 362.

\* Metals Research Laboratory, Carnegie Institute of Technology.

<sup>5</sup> *Trans. A.I.M.E.* (1929) **83**, 552.

<sup>6</sup> *Trans. A.I.M.E.* (1928) **78**, 390.

as a "heat of lattice loosening" on the basis that an energy quantity is needed to loosen the lattice to permit the movement of atoms, or to "loose" the atoms from their normal equilibrium lattice positions. There is quite a difference between a conception of this sort and the proposal of an effect of distortion on the rate of diffusion, a proposal that may be subject to experimental proof.

It seems obvious, however, that distortion should accelerate diffusion, for cold-work increases the average energy content of the atoms, lending them an additional potential mobility. Experimentally, however, the point is difficult to prove, for the effects of distortion are usually removed before diffusion has had time to proceed so far as to be demonstrable experimentally; this is the sense of the authors' findings. It is not true, however, that diffusion cannot proceed without distortion, as Desch<sup>7</sup> has said<sup>7</sup>, evidently following some early work by Hevesy<sup>8</sup> and by Elam<sup>9</sup>. Hevesy's early work was shown later by Seith<sup>10</sup> to be incorrect; the latter worker showed that radioactive lead will diffuse into lead single crystals, contrary to Hevesy's original findings—that the rate of this diffusion does not differ from that for polycrystalline lead, and that it was independent of previous mechanical treatment. This latter fact may not seem surprising owing to the low recovery and recrystallization temperature of lead, but the lack of dependence of the diffusion coefficient upon grain size does seem surprising in view of Langmuir's work on the diffusion of thorium in tungsten<sup>11</sup> and Giess and van Liempt on molybdenum in tungsten<sup>12</sup>.

There are many other observations that show that distortion caused by mechanical treatment is not a necessity for diffusion. Thus, zinc will readily diffuse out of single crystals of brass, and zinc vapor will diffuse into single crystals of copper, as shown in our laboratory recently. Similarly, recent work by Langmuir<sup>13</sup> and by Fonda, Young and Walker<sup>14</sup>, has shown that thorium will diffuse at a measurable rate through single crystals of tungsten. The metallurgist will also readily appreciate that the formation of a precipitate from a solid solution involves diffusion and that therefore diffusion must obtain within the single crystals making up the aggregate.

There can, therefore, be no doubt that diffusion can take place within what we may consider as an ordinary metal crystal, and that distortion in the usual meaning of the word is unnecessary; how far lattice imperfections enter into this process cannot be said, since experiments on this point are entirely lacking for metals, yet Smekal believes that they play the dominant role<sup>15</sup>.

That distortion can accelerate diffusion cannot be doubted, however, and in this respect we must differ from the authors. The few measurements available show that diffusion along grain boundaries is much more rapid than within crystals, and since slip planes are in many ways similar to grain boundaries we may expect a similar effect to be present in deformed metals. Apart from this argument, various experiments are available which show the effect of distortion on accelerating diffusion.

Such experiments have led Smekal to consider diffusion as a structure-sensitive property. It has been shown that diffusion in bismuth is greatly accelerated by strain and that the normal value may be reestablished by annealing; the diffusion of carbon in single crystals of tungsten made by the Pintsch process—which is known

<sup>7</sup> Reference of footnote 1.

<sup>8</sup> *Nature* (1925) **115**, 674.

<sup>9</sup> *Jnl. Inst. of Metals* (1930) **43**, 217.

<sup>10</sup> *Metallwirtschaft* (1934) **13**, 479.

<sup>11</sup> *Jnl. Franklin Inst.* (1934) **217**, 543.

<sup>12</sup> *Ztsch. anorg. Chem.* (1927) **168**, 107.

<sup>13</sup> Reference of footnote 11.

<sup>14</sup> *Physica* (1933) **4**, 1.

<sup>15</sup> *Handbuch der Physik*, **24**, II.

to make imperfect, porous crystals—was shown by Zwicker<sup>16</sup> to be much more rapid than in tungsten crystals made by deposition from the gaseous  $WCl_6$ ; furthermore Fonda, Young, and Walker<sup>17</sup> showed that bent Pintsch tungsten crystals exhibited a more rapid diffusion of thorium than undeformed crystals, but that subsequent annealing restored the diffusion velocity of the undeformed crystals.

The accelerating effect of cold-work on the rate of aging in age-hardening systems offers indirect evidence on this same point. Hone<sup>18</sup>, at the Carnegie Institute of Technology, and later Bucknall and Jenkins<sup>19</sup> in England showed that the rates of aging at different temperatures are related by an exponential function quite comparable to that for diffusion. It seems more than likely that the rate of diffusion is the primary factor in determining rates of age-hardening; the acceleration of the age-hardening by cold-work is thus indirect evidence for an acceleration of the rate of diffusion.

We thus have scattered evidence that crystal imperfections and distortion can accelerate diffusion, but also have evidence that diffusion does take place within the true crystal grain at least in several cases. Only in special cases, and by the use of special techniques can the first be demonstrated. So far as we know there is no justification for the statement that cold-work may impede diffusion.

Internal stress doubtless existed in the electroplated coatings used by the author, but it must be remembered that much of the line width observed prior to annealing probably originated in the very small crystals present; by no means the whole of the line width may be ascribed to strain, as Wood—who studied this problem thoroughly—has shown.

It might be noted that the doubling of the alloy lines in the copper-gold system— noted on page 94—probably originates in the heterogeneous nature of the intermediate alloys at 300° C. These intermediate phases are not formed at 500°, and at this temperature the alloys should be continuous in composition (and in  $a_0$ ) from copper to gold.

J. L. BURNS,\* Chicago, Ill. (written discussion).—As the authors have indicated, the effect of lattice distortion should be differentiated from the effect of cold-work upon diffusion, because the latter includes the former as well as other effects upon the crystal structure. It is frequently stated that cold-working assists homogenizing of alloys upon subsequent annealing. However, all of the lattice distortion is removed at the annealing temperature and so it would seem to be something else, which occurs during the working operation, that assists homogenizing.

The effect of cold-work upon diffusion in age-hardening systems is interesting. This is not easy to study because in most systems the alloy recrystallizes before diffusion takes place. Some age-hardening alloys do show diffusion below the temperature at which strain relief occurs—i.e., duralumin, Fe-C, and Fe-N systems—and so the effects may be studied.

There have been references in the literature to the effect of cold-work upon the diffusion of quenched duralumin. These state that plastic deformation increases the hardening rate. This has been shown to be true only for the early stages of aging, and not in the later. The explanation of this is probably associated with the obliteration of the incubation period by the cold deformation. An analogy between cold-work and certain cooling rates has been shown as regards their effect upon the initiation of the hardening.

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<sup>16</sup> *Physika* (1927) 7, 189.

<sup>17</sup> Reference of footnote 14.

<sup>18</sup> Thesis, Carnegie Inst. of Tech. (1934).

<sup>19</sup> *Jnl. Inst. of Metals* (1935).

\* Republic Steel Corporation.

It appears that some precipitation occurs during the working operation and this allows the hardening to begin immediately. If duralumin is cooled at a slower rate than water cooling and yet fast enough to create some supersaturation, no incubation period will ensue. Cold-work, therefore, allows the hardening to begin earlier, but decreases the final hardening due to aging. It would be concluded, then, that cold-work reduces the total diffusion.

The authors are to be congratulated for their method of attack, where the separation of lattice distortion from the other effects produced by cold-work has been made possible. It is through the separation of the various factors concerned in cold deformation that we may understand the mechanism of its effect upon diffusion.

S. TOUR,\* New York, N. Y.—This diffusion work of the authors is certainly very interesting. It is interesting particularly to note that their work was done on samples heated at these temperatures for 24 hr. We have found that diffusion in gold systems proceeds so rapidly that it is possible to study it metallographically. There is sufficient diffusion between gold and copper to find metallographically after 5 min. at 450° C. The same applies to the gold-nickel system and to the silver-copper system. In other words, these diffusions proceed at an enormous rate, at the start. How far it goes in the 24 hr., it is of course difficult to say. We have found that heating a deposit 0.001 in. thick of gold on nickel, at 450° C. for 15 min. is sufficient to diffuse enough nickel through that gold to change the color of the gold. That indicates a very rapid amount of diffusion of the nickel into the gold.

Metallographically, we have been unable to find any decided difference in the rate of diffusion of nickel into gold, whether the gold is deposited on severely cold-worked metal or on annealed metal. There is a decided difference in the appearance of the boundary line but there is no indication that the rate of diffusion is any more or any less.

The rates are so enormous at first that they would be difficult to measure. In annealed nickel, with rather coarse grains, it is quite evident that diffusion tends to follow grain boundaries. It would appear that the changes occurred first along the grain boundaries. In the coarse grain base the diffusion areas show as numerous "fingers" along the grain boundaries. In a severely cold-worked material there are very few of these long "fingers" of alloy but a fairly uniform layer of alloy develops. Heating an hour at 450° C. develops an alloy layer approximately two-thousandths of an inch thick. This indicates the speed of the diffusion.

I have pointed out these things in order to call attention to the availability of metallographic methods in studying diffusion, as many laboratories are not equipped for X-ray work.

R. M. BRICK,† New Haven, Conn.—Dr. Norton pointed out in one of his slides that in the gold-copper system crystal recovery precedes diffusion. Whether this is generally true, of course, would probably depend on the atomic energy of the two alloy components and on their atomic sizes. I wonder whether, by using a higher temperature, say 600° C., and studying the changes taking place over a time interval, the same results would have been obtained.

An interesting structure was recently observed at Hammond Laboratory. A supersaturated aluminum-magnesium alloy was cold-rolled to an 85 per cent reduction. On reheating at a low temperature, precipitation took place approximately a thousand times more rapidly than in strain-free material. Precipitation preceded recrystallization and the second phase was concentrated along the elongated original grain boundaries. As heating at the low temperature, 250° C., continued, new grains were formed

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\* Vice President, Lucius Pitkin, Inc.

† Hammond Laboratory, Yale University.

and the concentration of precipitate along the old boundaries eventually disappeared. In this case, the diffusion necessary for precipitation occurred long before recrystallization, at any rate, although perhaps not before crystal recovery.

J. T. NORTON.—I do not know that I can reply in detail to all the points that have been brought up. The discussions as a whole emphasize the confusion that exists as to the effect of cold-work. Many of the effects that have been discussed leave completely out of the picture the effect of lattice distortion as contrasted with the effect of grain fragmentation, the formation of new grain boundaries, and the formation of slip planes within the crystal grains.

The real reason for the application of X-ray methods to this problem was that it is the only method I know of to investigate the question of lattice strain in local regions, and of course the microscope tells one very little about that phase of the matter.

As far as the exponential diffusion-rate curve is concerned, it is a fact that is pretty well established, but it is not clear, in looking at the literature, how much of the information upon which this general picture is based has taken into account the effect of the previous condition of the samples. The greater part of the work has been done on annealed samples, which are strain-free, and much more must be done on the problem before we can see how the curve that applies to annealed samples will behave if the effect of strain and fragmentation are brought into the picture.

Of course we did not intend to indicate, and I do not believe we have said, that lack of distortion would entirely prevent diffusion. Everyone is familiar with the very slow diffusion rates that take place at low temperatures, at which lattice strain is not relieved, but we merely pointed out that the relief lattice strain apparently allows diffusion to take place at an increased rate.

I do think that one of the most important problems is to see whether we can separate in some way the effect of actual lattice distortion and the effect of grain fragmentation, both of which result from cold-work.

V. G. MOORADIAN AND J. T. NORTON (written discussion).—The results presented are of a preliminary nature but the authors feel that they indicate important possibilities of further work and hope that other investigators will contribute results along similar lines.



# Quenching Stresses and Precipitation Reaction in Aluminum-magnesium Alloys

BY R. M. BRICK,\* JUNIOR MEMBER, ARTHUR PHILLIPS†, MEMBER, AND A. J. SMITH‡,  
ASSOCIATE MEMBER A.I.M.E.

(Chicago Meeting, October, 1935)

A PREVIOUS publication<sup>1</sup>§ has described the effect of quenching stresses on the lattice parameter values of high-purity aluminum-copper alloys particularly with reference to the solution and precipitation of  $\text{CuAl}_2$ . A similar study has been made of the aluminum-rich aluminum-magnesium alloys. Attention has been directed in the present investigation to the magnitude of the quenching stresses as affected by the specimen size and shape, the number of solute atoms and the quenching rate. The effect of cooling stresses in causing plastic deformation or cracking has been considered in relation to the physical properties of the alloy. On reheating alloys in the two-phase field, the time required for precipitation to occur has been observed in connection with the degree of supersaturation, the rate of diffusion of the solute atoms as a function of the comparative atomic radii, degree of strain, temperature of reheating and grain size. A few qualitative comparisons on the relative effect of these factors have been drawn between the aluminum-copper alloys and the aluminum-magnesium alloys.

## STRAIN IN SOLID-SOLUTION ALLOYS

A 10 per cent magnesium alloy in the form of chill-cast bars was furnished by the Aluminum Company of America through the courtesy of L. W. Kempf. Additional alloys were prepared using aluminum (99.95 per cent Al) and high-grade magnesium. The alloys listed in Table 1 were melted in an Acheson graphite crucible under a flux of fused  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{NaCl}$ . Chill-cast rods were sealed under vacuum in Pyrex glass, homogenized several days at  $450^\circ \text{C}$ ., air-cooled and machined to rods of from  $\frac{1}{8}$  to  $\frac{3}{4}$ -in. dia. Metal powders taken from these rods with a fine-toothed saw were again sealed under vacuum in

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\* Research Assistant in Metallurgy, Yale University, New Haven, Conn.

† Professor of Metallurgy, Yale University.

‡ Graduate Student, Yale University.

§ References are at end of paper.

Pyrex, heated  $\frac{1}{2}$  hr. at  $450^{\circ}$  C. and air-cooled. The rods were also treated in a salt bath at the desired temperature for  $\frac{1}{2}$  hr. and cooled as later specified.

TABLE 1.—*Alloys Used in Test*  
Concentrations Expressed in Weight Percentages

Mg.....	1.8 <sup>a</sup>	4.0	5.6	6.0 <sup>a</sup>	8.2	9.98	10.2 <sup>a</sup>	11.5 <sup>a</sup>	14.5	17.2
Fe.....						0.035				
Si.....						0.030				
Cu.....						0.045				

<sup>a</sup>Signifies percentage of magnesium derived from X-ray data.

Lattice constant values of the alloys when in complete solid solution are shown in Fig. 1. The line drawn through the  $a_0$  values of the alloy

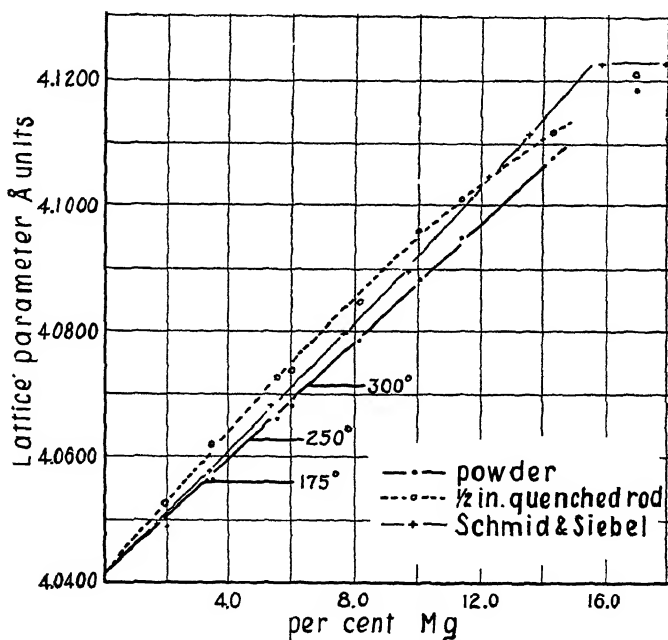


FIG. 1.—LATTICE PARAMETER VALUES OF AL-MG ALLOYS IN COMPLETE SOLID SOLUTION, TOGETHER WITH THREE LOW-TEMPERATURE HORIZONTALS.

powders probably shows the true change in parameter of the aluminum matrix with increasing magnesium content for alloys substantially free from strain. The composition factor is subject to some uncertainties owing to the possibility of losing magnesium by oxidation from oxygen dissolved in the liquid salt or by sublimation in vacuum. It is believed that this error was minimized by preparing the specimens after a homogeneous solid solution was attained and then removing the machining stresses by subsequent heat-treatments of relatively short duration.

The dotted line in Fig. 1 gives the parameter values of  $\frac{1}{2}$ -in. rods quenched in cold water, which normally show the maximum susceptibility to high quenching stresses. Also reproduced in Fig. 1 is the parameter-per cent magnesium line reported by Schmid and Siebel<sup>2</sup> on quenched 0.2-in. rods. It is probable that their  $a_0$  values are high as a result of the

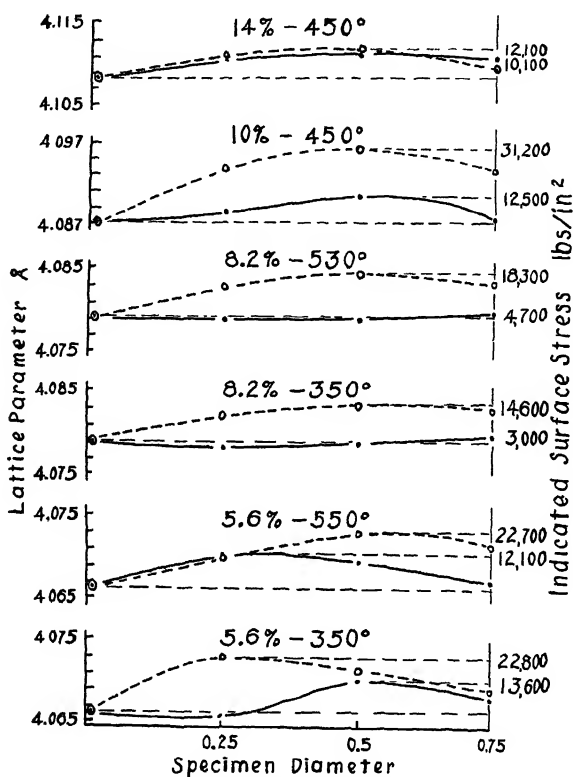


FIG. 2.—PARAMETER AND STRESS VALUES FOR RODS OF VARYING DIAMETER.

Dotted lines refer to alloy rods quenched in cold water and solid lines to rods cooled in still air.

presence of quenching strains. Further evidence on this point is offered in Fig. 2, in which are plotted the parameter values found for different sizes of specimens when quenched and when cooled in still air. The curves indicate that: (1) powders are least subject to strain, (2) the  $\frac{1}{2}$ -in. rods quenched in cold water show (with one questionable exception) the greatest strain and (3) rods even when air-cooled may have considerable surface stresses.

The magnitude of the stresses present in the surface layers of the rods is related to the strain, as given by the lattice parameter difference, through an equation developed by C. S. Barrett<sup>3</sup>. Using his formula, the

stresses present in these rods have been calculated and the maximum values found are also indicated in Fig. 2. The numerical value of these stress figures is contingent on the assumption that the powders are free from stress. Uncertainty on this point, together with the errors inherent in the lattice constant determination somewhat reduces the accuracy of the calculated stress values.

The stresses developed in a quenched rod are determined by the specimen size, composition and cooling rate. The effect of size has already been considered. The cooling rate depends on: (1) the temperature and physical characteristics of the cooling medium, (2) the specimen size and temperature and (3) the thermal properties of the alloy. From the data in Table 2 and that shown in Fig. 2, it seems certain that in general the stresses are higher with more drastic quenching; i.e., colder media and higher quenching temperatures. Considering similar rods of aluminum-copper alloys and aluminum-magnesium alloys cooled from the same temperature and in the same medium, it has been noted that the aluminum-magnesium alloy generally cooled slightly faster than the aluminum-copper. This qualitative observation seems generally true but without specific information respecting the relative thermal conductivities and heat capacities of the two alloys, no reason for the difference can be definitely formulated.

TABLE 2.—*Stresses Found in 10 Per Cent Magnesium Rods on Cooling from a Solution Treatment*

Diameter of Rod, In.	Cooling Medium	Quenching Temperature		
		400° C.	450° C.	500° C.
		Stresses, Lb. per Sq. In.		
1/2	Cold water	20,600	31,600	32,300
1/2	Boiling water			22,700
1/2	Still air	11,800	14,900	10,200
3/4	Cold water	8,000	20,400	20,500
3/4	Boiling water			17,500
3/4	Still air	3,100	1,500	3,100

Finally, the magnitude of the quenching stresses is dependent on the composition or the concentration of solute atoms, neglecting the effect of impurities. The data of Table 3, an average of several stress determinations by parameter measurements, suggest that for a given atomic content of either copper or magnesium dissolved in aluminum, the stresses found in quenched 1/2-in. rods are of approximately the same order of magnitude. However, the parameter change of the aluminum

matrix per unit concentration of solute atoms may be a more logical basis for comparison. The table indicates that for the two alloys under consideration, the stress per unit  $a_0$  change is practically identical. An observation on a single pair of alloys cannot perhaps be accorded too much weight and, even though the conclusion should be found to be correct, the effect of possible inherent differences in the cooling rates of various alloys would limit the usefulness of the concept.

TABLE 3.—Average of Stress Determinations by Parameter Measurements

Alloy	Weight Per Cent	Atomic Per Cent	$a_0$ Change per 1 Atomic Per Cent Solute	Change in $a_0$ at Saturation	Stress, Lb. per Sq. In.	
					Total	Per 0.0001Å Change of Al $a_0$ Value
Cu. . . . .	5.4	1.9	-0.0060	-0.0125	11,500	127
Mg. . . . .	1.8	1.9	+0.0046	+0.0750	11,300	130

It has been found in previous work that under similar physical conditions the quenching stresses in aluminum-copper alloys increase nearly linearly with the copper content. If the magnitude of the quenching stresses is related to the change in parameter of the matrix lattice per unit concentration of solute atoms, and assuming the linear relationship to continue, the table indicates that the very large change in parameter possible with magnesium might result in the development of stresses of the order of 100,000 lb. per sq. in. for the fully saturated alloy. Since the maximum strength of these alloys varies from 25,000 to 50,000 lb. per sq. in., stresses of the above magnitude should result in localized failures. Such failures are found, as a matter of fact, in the form of surface cracks in all alloys containing more than about 4.0 per cent magnesium. When the rods were reheated, the very fluid salt penetrated the most minute cracks so that after cooling, washing and drying, the now aqueous salt solution comes to the surface of the rod and dries, delineating the crack with a thin white line. The cracks appear almost equally in the longitudinal and tangential directions (see Fig. 3) in accordance with the well-known distribution of stresses in quenched rods. A  $\frac{1}{2}$ -in. rod of which 15 per cent magnesium alloy, was inadvertently dropped on the floor after precipitation at 250° C. was complete, broke in several pieces. Each section clearly showed the original quenching cracks extending to a depth of about half the radius of the rod; in other words, to the neutral axis of stress (Kempf<sup>4</sup>). The smooth conchoidal surfaces of the cracks indicated that they were transcrystalline and must have formed when the rod was relatively cold. It is probable that the cracks are completely formed in the course of the quenching operation, since,

particularly in the higher magnesium content alloys, 12 per cent or above, no significant drop in parameter has been found on aging at room temperatures. In the lower magnesium content alloys, the parameter values of the quenched rods have been found to decrease slightly on aging, a drop comparable to that found in the aluminum-copper alloys<sup>1</sup>. The decrease is only slightly greater than the limit of error in the lattice constant measurement and apparently is caused by minor stress readjustments due to creep or the further propagation of cracks.

Although the surface stresses normally are expressed as being in compression, the atoms actually have been pulled apart as by a tensile force and the failure is a crack. In the center of the quenched rods where the stresses are normally said to be acting in tension, the atoms are actually under compression. No cracks have been found in the centers of the rods, probably because the compressive strength of the alloys is

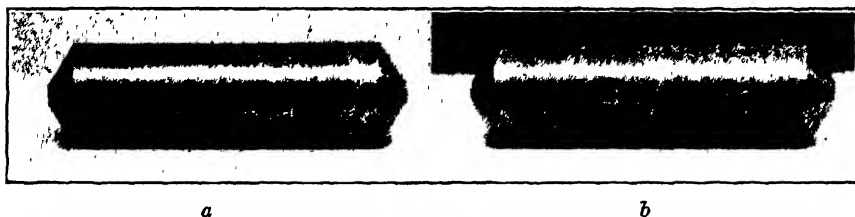


Fig. 3.—EFFECT OF REPEATED QUENCHINGS FROM 540° C. ON  $\frac{1}{2}$ -INCH ALUMINUM-MAGNESIUM RODS.

a. 4.0 per cent Mg surface shows plastic deformation.

b. 17.2 per cent Mg surface shows cracks but no deformation.

so much greater and at the same time the surface failures would permit a certain atomic readjustment and partial relief of stresses at the centers of the rods.

From the foregoing considerations, it is apparent that the maximum stress obtained on quenching a particular rod is limited by the physical properties of the material. The strongest aluminum-magnesium alloy is that one containing about 10 per cent magnesium and the highest stress values found in the course of this work, 32,000 lb. per sq. in., were on this alloy. It is interesting to note that in Fig. 1, assuming the maximum solubility limit to be about 15.5 per cent magnesium, as shown by Schmid and Siebel, the 17.2 per cent magnesium rod has a stress of 32,000 lb. per sq. in. while the powder shows a stress of 24,000 lb. per sq. in. While another explanation of the high  $\alpha_0$  value found for the powder may be possible, it is on the basis of this result that doubt must again be emphasized as to the equilibrium  $\alpha_0$  values for all of these alloys and the stress values derived therefrom.

In an attempt to determine the maximum limit of quenching stresses, three alloy rods were repeatedly quenched in water from 540° C., and X-rayed, using a reheating time of 50 sec. in the salt bath at 540° C.

The surfaces of both a 5.4 per cent copper-alloy rod and a 4.0 magnesium-alloy rod gradually assumed a distorted appearance which, after 20 quenchings, were very similar to the surface of a bar heavily stretched in a tensile test (see Fig. 3). The stress evidently had developed to a point above the elastic limit of the alloy but within the tensile strength limit, therefore instead of cracking, plastic deformation of the surface had occurred. This was further proved by a very noticeable refinement of the grain structure through recrystallization, as shown by the X-ray reflection lines and by micrographic examination. Careful micrometric measurements of the dimensions of the rods in the course of the 20 quenchings indicated that the length of the 4.0 per cent magnesium-alloy rod decreased from 1.7657 in. to 1.7638 in. while the diameter increased from 0.4990 in. to 0.5000 in. The same treatments given to a 17.2 per cent magnesium rod increased the depth and frequency of the cracks but did not measurably affect the length or diameter of the rod.

Whether a rod shows deformation or cracking seems to depend on the potential stresses, as affected by composition, size and cooling rate, in relation to the yield point, tensile strength and other physical properties of the alloy; these same factors probably will also determine the depth of the cracks. Finally, the same considerations seem to offer a satisfactory explanation of the course of the parameter-per cent magnesium line for the  $\frac{1}{2}$ -in. quenched rods shown in Fig. 1.

It has been noticed that in numerous investigations involving lattice constant determinations, specimens with flat surfaces, either sheet or disks, were employed. The experiments on several alloy disks as shown in the data of Table 4 were performed with the hope of defining the stress distribution on flat surfaces. However, no definite conclusions in this respect can be formed from these limited data, and the only comment possible is that stresses were present as shown by both the parameter values and by cracking across the flat surfaces of the higher magnesium-content alloys.

TABLE 4.—*The  $a_0$  Values Obtained by X-raying Flat Al-Mg Disks,  $\frac{1}{2}$  Inch Thick by  $\frac{3}{4}$ -inch Diameter, after Quenching from 450° C. in Cold Water*

Values for the Same Alloy Powders Are Shown for Comparison

Point X-rayed	Per Cent Magnesium			
	4.0	6.0	10.2	11.5
Powder.....	4.0566	4.0678	4.0877	4.0946
Flat surface, center.....	4.0618	4.0724	4.0916	4.0956
Flat surface, edge.....	4.0605	4.0719	4.0913	4.0985
Cylindrical surface.....	4.0616	4.0732	4.0907	4.0998

## PRECIPITATION IN ALUMINUM-MAGNESIUM ALLOYS

The breakdown of the supersaturated solid solution in aluminum-magnesium alloys is accompanied by the precipitation of the compound  $Mg_2Al_3$  together with a corresponding change in the parameter of the aluminum matrix. To obtain the usual reaction curve, the  $a_0$  values of the solid solution have been plotted against the time of reheating at the lower temperature; i.e., in the two-phase field. The  $a_0$  values show a slight drop in the early stages of reheating, probably owing to a partial

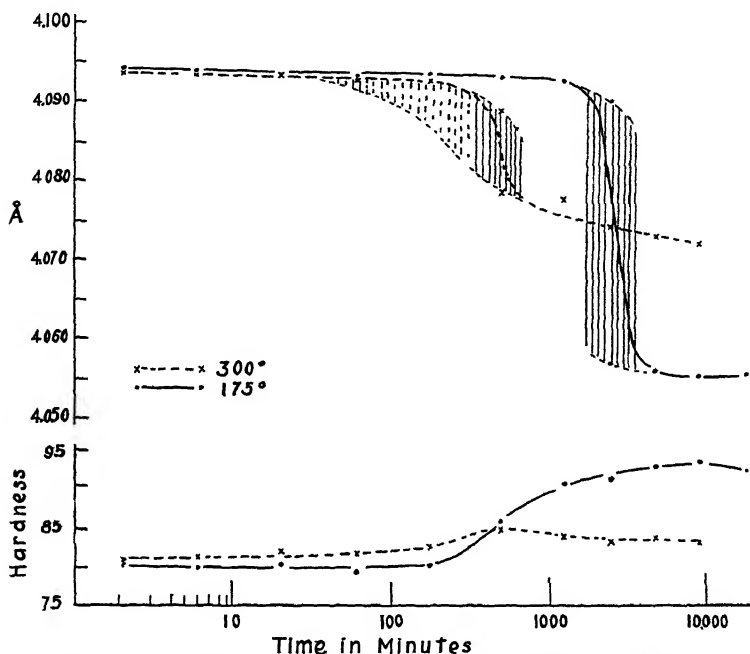


FIG. 4.—REACTION CURVES FOR 10 PER CENT MG ALLOY  $\frac{1}{2}$ -INCH QUENCHED RODS AT DESIGNATED TEMPERATURES.

Heavily shaded area indicates approximate precipitation range found by X-ray determinations and lightly shaded area indicates range of visible precipitates in microstructure.

relief of the solution quenching stresses. The actual precipitation reaction is indicated on the X-ray photographs of these alloys by the appearance of new lines having approximately the spacing of the lattice stable at the lower temperature. The lines of the original lattice decrease in intensity and those of the new lattice increase in intensity until precipitation is practically complete. Two typical reaction curves have been reproduced in Fig. 4. Although the actual process is more accurately portrayed by the shaded area, other figures will show only the line drawn through the center of this area, spaced approximately according to the relative intensities of the initial and final lattice reflections.



The time required for the precipitation reaction to be completed is in general a function of the relative driving forces and the diffusion rates. The following data are presented in an attempt to evaluate these two active factors. Fig. 5 shows the reaction rate at 250° C. of an aluminum-copper alloy containing nearly the maximum solution content of copper (5.4 wt. per cent or 1.9 at. per cent). Contrasted with this are the reaction curves for an aluminum-magnesium alloy having the maximum solution content of Mg (16.0 at. per cent) and an alloy having approximately the same degree of supersaturation; i.e., about 1.8 at. per cent of precipitating solute. In the latter case, under somewhat similar conditions of strain, temperature and grain size, the copper alloy precipitates

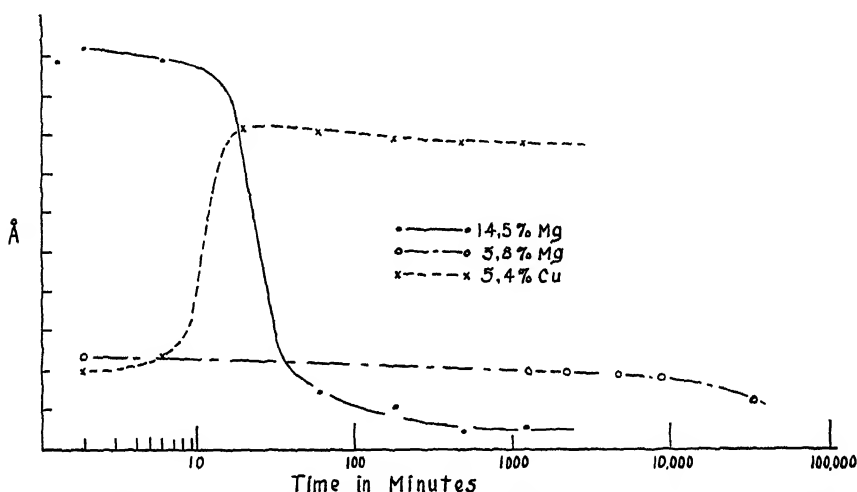


FIG. 5.—REACTION CURVES AT 250° C. FOR DESIGNATED ALLOYS IN FORM OF  $\frac{1}{2}$ -INCH QUENCHED RODS.

Scale of  $\alpha_0$  values for Al-Cu alloy has been enlarged and displaced vertically to facilitate comparison of rates.

completely in about 20 min. while a like amount of magnesium has not completely precipitated at the end of 1000 hr. The profound difference in the reaction rate cannot be entirely explained at present since no information is available on the relative energies of formation for the two compounds or the driving forces that may be acting in this direction. Although the ordinate scale of  $\alpha_0$  values in Fig. 5 has been changed and shifted for the copper alloy, the total parameter change in each case is nearly the same and cannot be a factor, as it seems to be in determining the magnitude of quenching stresses.

The proportion of the maximum solution content of solute atoms present may be of some significance. It will be seen that in Fig. 5, the fully saturated alloys of copper and magnesium both precipitated at substantially the same time. The difference found, only a few minutes,

may be entirely based on slight differences in stresses present in the two alloys, or it may be that the similarity in rates is entirely coincidental.

The contrast in the rate of precipitation for the copper and magnesium alloys having the same degree of supersaturation can be at least partly attributed to the relative diffusion rates of the two alloy elements. Wyckoff gives the following figures for their atomic radii: Mg, 1.66 Å.; Al, 1.43 Å.; Cu, 1.27 Å. Although no definite physical significance should be attached to the actual values given, there seems to be little

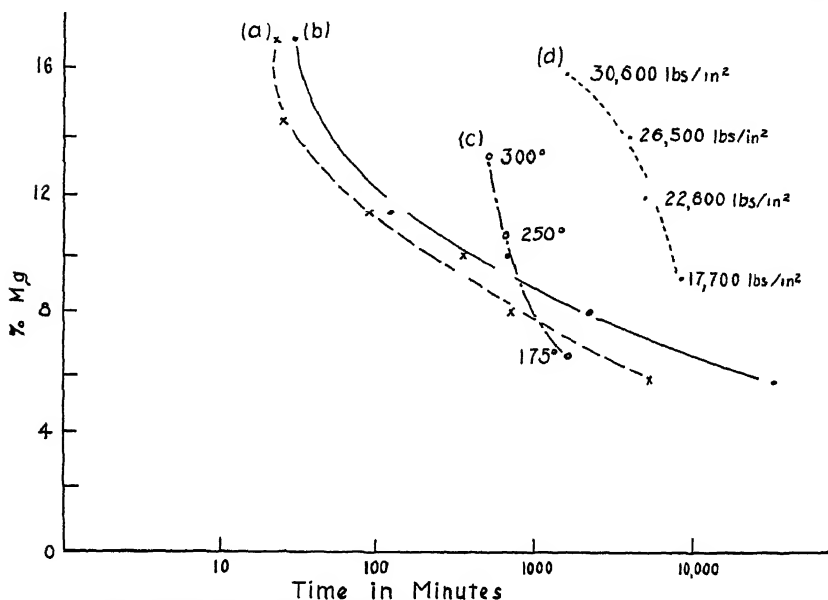


FIG. 6.—TIME REQUIRED FOR PRECIPITATION IN AL-MG ALLOYS TO BE APPROXIMATELY HALF COMPLETED PLOTTED AGAINST INDICATED VARIABLES.

- a. Powders of various Mg content treated at 250° C.
- b.  $\frac{1}{2}$ -in. quenched rods as above at 250° C.
- c. A 10 per cent Mg alloy in form of  $\frac{1}{2}$ -in. quenched rods treated at 300°, 250° and 175° C.
- d. A 10 per cent Mg alloy in form of  $\frac{1}{2}$ -in. rods cooled to give various stress values and treated at 175° C.

doubt that copper atoms can diffuse through aluminum much more readily than the larger magnesium atoms. The speed of precipitation for the fully saturated magnesium alloy can be explained on the basis of a considerably greater driving force and the shorter distances necessary for the magnesium atoms to travel owing to the considerably greater number of nuclei formed.

Rather than plot the large number of reaction-rate curves obtained in this work, the less confusing expedient has been adopted of plotting the reaction time against the different variables studied. The reaction time used in the plots has been arbitrarily chosen as that time when the parameter curve indicates that the transformation is half completed, in

other words, when the reflections of the old and new lattices are approximately equal in intensity. On this basis, Fig. 6 has been drawn to show:

Curves *a* and *b*, the marked increase in the reaction time at 250° C. for powders and rods respectively, with decrease in the degree of supersaturation,

Curve *c*, the increase in time required for a 10 per cent Mg alloy to precipitate as the reaction temperature is dropped from 300° to 175° C., and

Curve *d*, the effect of strain in the range 17,000 to 30,000 lb. per sq. in. on the reaction time for a 10 per cent Mg rod at 175° C.

With regard to the last point, the figure shows that the alloy powders, relatively free from quenching strain, transformed in every case before the ½-in. quenched rods, which were known to be severely stressed. The explanation of this anomalous result apparently lies in the grain-size differences. While grain-size differences in the aluminum-copper alloys had only a slight effect on the reaction rate, the aluminum-magnesium alloys seem to be quite sensitive in this respect. The powders had an extremely small grain size as compared to the chill-cast rods. The data below give some indication of the influence of grain size on the precipitation rate in an 8.4 per cent Mg alloy reheated at 250° C. It might be pertinent to point out here that the effect of grain size on the precipitation rate, especially in comparing the copper and magnesium alloys, is at least partly explicable in terms of the diffusion rates and distances required.

Per Cent Mg	Average Grain Diameter, In.	Reaction Time (50 Per Cent Completed), Hr.
8.4	0.001	20
8.4	0.005	45
8.4	0.060	100

Fink and Smith<sup>5</sup> recently reported that precipitates may form in aluminum-magnesium alloys to a size easily visible in the microscope without any change in the parameter of the aluminum matrix. This observation suggests that the aluminum matrix atoms may remain in an abnormally spaced arrangement after the removal of solute atoms. Since all the data in the present study have been based on parameter determinations, it was necessary to evaluate more completely the significance of their results.

An 11.5 per cent Mg alloy rod after a solution treatment was reheated for 80 min. at 250° C. The microstructure showed an appreciable amount of precipitate while the normal X-ray exposure gave the original solution  $\alpha_0$  value, a result similar to those reported by Fink and Smith. The same specimen was then exposed for 4 hr. instead of the usual

40 min. and the X-ray film now showed, on close examination, indications of a new lattice. In Fig. 7, the (333) doublet of this film has been reproduced with arrows pointing to the light and somewhat blurred spots which indicate a shift towards the new lattice parameter. A similar long exposure of the flat polished surface used for the micrographic examination is also reproduced in Fig. 7 and here again the new (333) doublet is faintly but distinctly visible. Similar results were obtained on a 10 per cent magnesium alloy rod heated 3 hr. at 250° C.

This characteristic of the aluminum-magnesium alloys is probably related to the slowness of the diffusion of the large magnesium atoms through the aluminum matrix. In the aluminum-copper alloys, the comparatively small copper atoms apparently diffuse quite readily through the matrix to the  $\text{CuAl}_2$  nuclei and therefore, during precipita-



FIG. 7.—THE (333) DOUBLETS FOUND AFTER LONG X-RAY EXPOSURE OF ALLOYS, WHICH HAD VISIBLE PRECIPITATES BUT SHOWED NO PARAMETER CHANGE AFTER NORMAL EXPOSURE.

a. Surface of rod.

b. Flat polished surface showing precipitate.

tion, the X-ray photograms of these alloys exhibit a wide diffuse band, which includes at least part of the concentration range between the initial and final states. However, during the precipitation of  $\text{Mg}_2\text{Al}_3$  in the aluminum-magnesium alloys, the part of the supersaturated solid solution that has been depleted of magnesium is decidedly more limited to the proximity of the precipitate, and it is quite possible that appreciable volumes of the matrix remain with their full quota of solute atoms. The X-ray photogram of an alloy in this condition would show, as actually found, reflection lines of both the original and new lattices with only a slight shading in between. Wiest<sup>6</sup> and others have pointed out that there is no significant difference between reactions appearing in the two different forms mentioned. Although apparently precipitation has occurred without any parameter change, it seems probable that this result is simply another indication of the insensitivity of the back-reflection X-ray method to small quantities of different phases or parts of phases with different  $a_0$  values.

Further information on the general subject of parameter changes in connection with precipitation is perhaps revealed by the experiment mentioned on page 7, in which several alloy rods were repeatedly quenched from 540° C. A micrographic examination showed that precipitation had occurred in all three rods, presumably during the rapid

reheating in the salt bath. Since 4.0 per cent magnesium is soluble in aluminum at all temperatures above 240° C., the precipitate found in the alloy rod of this composition may be attributed to the decrease in solubility resulting from the deformation. It has been previously observed<sup>7</sup> that deformation resulting from polishing operations on aluminum-copper alloys decreases the solubility of copper in aluminum and causes precipitation under abnormal conditions. The same reasoning may or may not be applicable to the 5.4 per cent copper and the 17.2 per cent magnesium-alloy rods. At any rate, it was noticed that contrary to the observations on rods reheated in the two-phase field, the X-ray reflection lines here remained fairly sharp but displaced in the direction showing precipitation. It seems possible that the stress or strain present in the rods had considerably increased the diffusion rate, as would be expected, and that, consequently, a general adjustment of the matrix concentration took place almost simultaneously with precipitation. The data of Table 5 indicate the actual values found.

TABLE 5.—*Parameter Changes in Alloy Rods after Repeated Quenchings from 540° C. with a 50-second Heating Interval, Which Resulted in Partial Precipitation*

Quench	5.4 Per Cent Cu	4.0 Per Cent Mg	17.2 Per Cent Mg
Original . . . . .	4.0332	4.0618	4.1207
Twentieth . . . . .	4.0370	4.0606 <sup>a</sup>	4.1102

<sup>a</sup> There was less precipitate near the surface of this rod, owing to the more rapid heating here and the consequent opportunities for re-solution.

In addition to the results obtained on these rods, it was found that a 5.0 per cent copper alloy strip, rolled after a solution treatment to a 50 per cent reduction in area and reheated 10 sec. at 540° C. had considerable precipitate present and that the X-ray photogram indicated that only 2.0 per cent copper was in solution although, owing again to the rapid diffusion rate, the reflection lines were quite sharp.

This interpretation of the results reported by Fink and Smith would seem to justify the use of parameter measurements in the study of precipitation reaction rates where due recognition is accorded the lack of sensitivity inherent in the method. While the start of the reaction cannot be timed accurately, the measurements should indicate fairly closely the midpoint of precipitation where initial and final lattice reflections are of approximately the same intensity. The true starting point of the reaction presumably occurs at a time soon after reheating is begun, shown in Fig. 4 as the lightly shaded area in which visible precipitates were found in the microstructure. Judging from the remarks published by Talbot and Norton<sup>8</sup>, it would appear that

these workers have views that are in general agreement with those expressed above.

### PRECIPITATION IN ALUMINUM-COPPER ALLOYS

The precipitation of  $\text{CuAl}_2$  in quenched aluminum-copper alloys has been studied at temperatures lower than those employed in a previous work<sup>1</sup>. Fig. 8 shows that at 215° C. the hardening of a 5.0 per cent copper alloy rod may be definitely attributed to precipitation. At 140° C., the hardness of similar alloy rods has apparently reached a

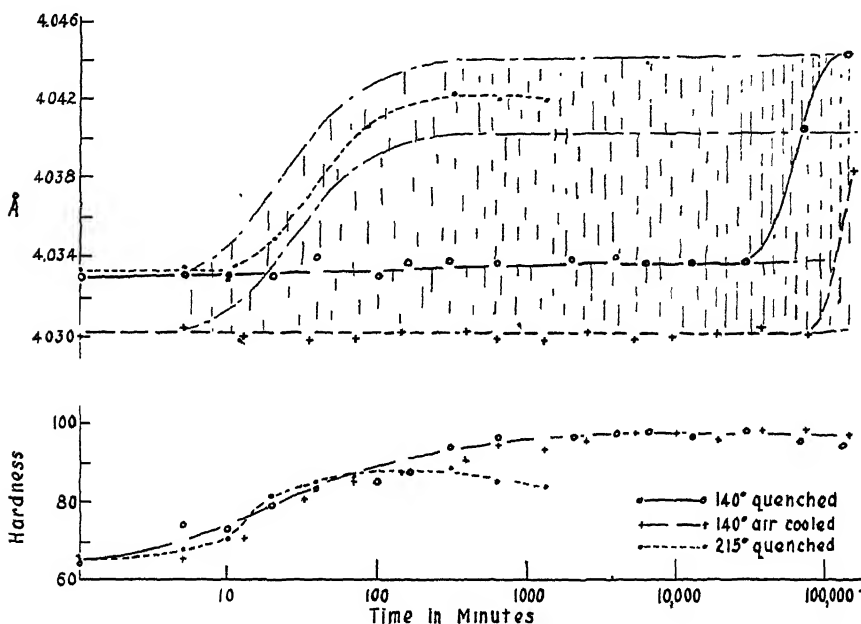


FIG. 8.—HARDNESS AND PARAMETER CHANGES OBSERVED FOR 5.0 PER CENT CU ALLOY  $\frac{1}{2}$ -INCH RODS ON REHEATING AT INDICATED TEMPERATURES AFTER SOLUTION TREATMENT.

maximum while the  $\alpha_0$  value is still predominantly that of the original solid solution. It should be remarked, however, that after holding the rod for only 10 min. at temperature, the X-ray reflection lines exhibited a diffuseness in the direction of precipitation and that after a total time of 53 days at 140° C. the photograms indicated that a considerable part of the solid solution had lost copper by precipitation. On the basis of the general explanation offered by Norton<sup>9</sup> for these phenomena i.e., a hardness due to "knot" formation and a separate hardness related to precipitation, it would seem that in the binary aluminum-copper alloys the principal hardening effect may be attributed to precipitation, particularly in view of the fact that considerably greater hardness is attained at 140° C. than at room temperatures. In the aluminum-magnesium

alloys, practically all of the hardening has been found to be associated with precipitation as indicated by Fig. 4 and confirmed by micrographic examinations. Since the results of Fink and Smith have revealed the lack of sensitivity of X-ray parameter measurements to localized matrix  $a_0$  variations, the absence of parameter changes or even of line broadening cannot be construed as proof positive that no precipitation has occurred. In fact, it may be suggested that these considerations eliminate the necessity for the concept of "knot" hardening.

### SUMMARY

1. Other factors being equal, the stresses in quenched aluminum-alloy rods seem to be a function of the difference between the parameter of the alloy and that of pure aluminum as related to the actual concentration of solute atoms, either copper or magnesium.

2. In the aluminum-magnesium alloys where up to 16 atomic per cent of magnesium is soluble with a correspondingly large total parameter change of about 0.0750 Å., the quenching stresses may greatly exceed the strength of the metal, thereby causing plastic deformation or cracking. For this reason, the maximum measured stress is limited by the physical properties of the alloy. The highest stress values found in this work were of about 32,000 lb. per sq. in. for a 10 per cent magnesium alloy in the form of a quenched  $\frac{1}{2}$ -in. rod.

3. All actual stress values derived from parameter measurements are subject to the uncertainties of obtaining the equilibrium, strain-free  $a_0$  value of the alloy.

4. The precipitation reaction in aluminum-copper or aluminum-magnesium alloys proceeds at about the same rate for fully saturated solutions. However, where the same concentration of solute atoms, 1.8 per cent, is precipitating, the copper alloy transforms completely in about 20 min. as compared to the period of over 1000 hr. required for the magnesium alloy. The difference is caused in part, at least, by the difference in the diffusion rates of the relatively large magnesium atoms as compared to the smaller copper atoms.

5. The effect of temperature, strain and grain size on the precipitation rates has been briefly considered. It seems probable that each of these factors changes the precipitation rate in part, as it affects the diffusion rate of the solute atoms.

6. Although precipitates were visible in the early stages of reheating of the supersaturated aluminum-magnesium solid solutions without any apparent parameter change, as reported by Fink and Smith, it was found that an extremely long X-ray exposure would reveal traces of the new lattice. Where precipitation occurs in strained metal, through which the solute atoms can more readily diffuse, the lattice constant changes throughout the solid-solution matrix.

7. The aluminum-copper precipitation reaction in the range from 140° to 325° C. exhibits a hardness maximum just before the time when precipitation, as shown by X-ray photograms, is complete. In the aluminum-magnesium solid solutions reheated in the range from 175° to 300° C., the hardness peak was observed after precipitation was entirely complete. The lack of sensitivity of X-ray back-reflection method,<sup>5</sup> however, precludes the use of parameter determinations in studies of the early stages of hardening or of precipitation in other than perhaps severely worked alloys.

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## DISCUSSION

(Gerald Edmunds presiding)

J. T. NORTON,\* Cambridge, Mass. (written discussion).—Just a few points in connection with this interesting paper warrant discussion, in view of some experiments that have been carried out at M.I.T. on magnesium-rich aluminum alloys, very much along the line of the results reported by Fink and Smith recently. The matter of quenching strains was studied carefully in view of these results. Experiments were made on flat disks rather than cylindrical rods; disks of 5/8-in. dia. and varying thicknesses were quenched at the same time, under the same conditions, and measurements made, and no effect of quenching strains was observed. We made an attempt to compare the parameter measurements on these disks with powders of the same composition, but we were not able to heat-treat the powder successfully without an appreciable loss of magnesium, and the results were very erratic, not at all satisfactory. I do not think the question is solved, but it seems to indicate that the effect of quenching strains is much less in these magnesium-rich alloys.

The aging results, while incomplete, show no evidence of knot formation. The X-ray photograms indicate local precipitation by the appearance of a second set of lines, but this appearance even with very long exposures is much later than the beginning of precipitation, as shown by resistance and dilatometer measurements and by the microscope. The alloys were difficult to homogenize but it seemed that the

\* Associate Professor, Physics and Metals, Massachusetts Institute of Technology.



more homogeneous the composition before quenching, the more uniformly the precipitation took place within grains. The visual precipitation under the microscope seemed to be at the grain boundaries. Experiments on fine powders and single crystals are now in progress.

The X-ray evidence in these alloys is definitely characteristic of a system in which local precipitation takes place and the situation can be immediately recognized from the appearance of the photograms. Under such circumstances, the X-ray method is not satisfactory for determining the time at which precipitation begins.

R. M. BRICK.—In regard to the quenching stresses, some experiments on disks were described in the paper. The results were somewhat variable although stresses of considerable magnitude were present since cracks occurred across the flat surface of the disk. I think stresses would probably be more easily recognized on cylindrical rods than on flat disks.

Dr. Norton's evidence on precipitation, as noted visually sooner than could be found by X-ray, is very interesting. I do not believe there is any real disagreement on this point, and Dr. Norton's results serve to confirm the previous observations on the insensitivity of the X-ray method.

## Theory and Use of the Metallurgical Polarization Microscope\*

BY RUSSELL W. DAYTON†

(New York Meeting, February, 1935)

THE metallurgical polarization microscope has been utilized in several researches in the last few years, thus attaining a fair degree of prominence, but little has been written in a manner suitable to a metallurgist concerning the theory of this instrument. In this investigation the theory was carefully studied, and the results are presented here in a detailed manner, yet as simply as possible. The theory is discussed with particular reference to the three chief functions of the instrument: (1) determination of anisotropy; (2) effect of strain; and (3) identification of inclusions. Each of these is investigated experimentally, with especial attention to the mechanism of producing any effect. Where possible, the discussion is supplemented by photomicrographs. The instrument used had numerous defects as a polarization microscope; these and their remedies are discussed.

In the microscopic study of transparent mineral sections (chalcography) the use of polarized light has aided tremendously in the identification of a mineral. The determination of strain in transparent substances (photoelasticity) by the use of polarized light has lately become a commercial process, used in testing finished glass articles.

The success of the use of polarized light with opaque materials has not been so great. The magnitude of the effects obtained is much less than that of the corresponding effects with transparent materials, and the mechanical difficulties are much greater. Königsberger,<sup>(1)†</sup> in 1909, was the first to apply polarized light to the microscopic study of opaque substances; Endell and Hanemann<sup>(2)</sup> were the next, in 1913. In 1919 and 1920, Wright<sup>(3,4)</sup> prepared two papers on the subject. In the first he developed the detailed mathematical theory from the viewpoint of the electromagnetic theory of light, and in the second described the various methods in use, giving improvements of his own. Schwarz<sup>(5)</sup>

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\* A thesis presented by the author to the Rensselaer Polytechnic Institute for the degree of Doctor of Philosophy. Manuscript received at the office of the Institute July 6, 1934.

† Research Metallurgist, Battelle Memorial Institute, Columbus, Ohio.

‡ References are at the end of the paper.

investigated the effects obtained with metals, using an instrument designed and constructed by Reichert. The features of this microscope and its operation are described by Primrose.<sup>(6)</sup> In the last few years, several investigators<sup>(7,8,9)</sup> have applied the method to their researches, and in each it was in some way found useful.

Little has been written concerning the theory of a metallurgical polarization microscope. The details concerning it must be sifted from a large amount of irrelevant material found in texts on optics<sup>(10,11)</sup> or mineralogy<sup>(12)</sup> and in the preceding references. The only detailed article on the involved theory<sup>(3)</sup> is mathematical, and to understand it the reader must possess a knowledge of the electromagnetic theory of light.

The first part of this paper, therefore, is devoted to a detailed but simple explanation of the principles involved. In the latter part, an experimental study is made of the functioning of the instrument.

### GENERAL THEORY

Light, for the purposes of this discussion, may be considered as a disturbance in the ether in which the particles transmitting it vibrate at right angles to the direction of propagation of the light. These vibrations may take place in any direction in the plane perpendicular to the motion of the light. Light in which all these vibrations are in one direction is called plane polarized light. The plane including this direction and the direction of motion of the light ray will be called the plane of polarization.

Ordinary light is unpolarized, the direction of vibration being entirely random. To polarize such light, a device such as a nicol prism is used, or others that perform similarly. Such a prism is made of a substance of which the internal structure is such that it decomposes into two rays every light vibration it transmits, both plane polarized and in planes at right angles to each other. These two rays travel at different speeds through the substance, so on entering it are refracted differently. (Such a substance is called doubly refracting.) It is possible, by a proper selection of angles in a prism of a doubly refracting substance, to eliminate one of these plane polarized rays by internal reflection, as by a nicol prism.

This prism will pass only light polarized in one plane. The total intensity of light transmitted is only half that of the entering unpolarized light, the other half being eliminated by the total reflection. If one of these prisms is used to polarize ordinary light, it is called a polarizer. If a nicol prism is used to examine light and determine whether it is plane polarized, it is called an analyzer. A polarizer and an analyzer can be set with their planes of polarization at right angles to each other, in which position they transmit no light. This position is called that of

"crossed nicols." If they are set with their planes of polarization parallel, the analyzer transmits all the light that the polarizer does, and this position is called that of "parallel nicols."

Fig. 1 shows the optical arrangement in the microscope used. It is an inverted type adapted for use with polarized light. Critical illumination is used in this instrument, which means that the source of light is focused on the specimen 12 by means of the condensing lens 2,

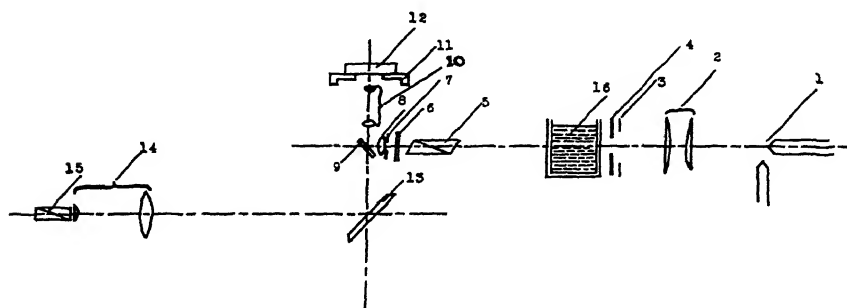


FIG. 1.—OUTLINE OF APPARATUS IN INVERTED METALLOSCOPE ADAPTED FOR USE WITH POLARIZED LIGHT.

- |                       |                           |                      |
|-----------------------|---------------------------|----------------------|
| 1. Arc lamp.          | 7. Field diaphragm.       | 12. Specimen.        |
| 2. Condensing lenses. | 8. Field lens.            | 13. Stellite mirror. |
| 3. Iris diaphragm.    | 9. Plane glass reflector. | 14. Eyepiece.        |
| 4. Special diaphragm. | 10. Objective.            | 15. Analyzer.        |
| 5. Polarizer.         | 11. Rotating stage.       | 16. Water cell.      |
| 6. Selenite plate.    |                           |                      |

the field lens 9 and the objective 10. This is accomplished by proper selection of the field and condensing lenses. The field lens has such a focal length that it will form an image on the back lens of the objective of the iris diaphragm or of anything else placed at that same point. In this way, the iris diaphragm can control the part of the aperture of the objective that is used, by controlling the area of the back lens that is filled with light.

The definitions of the terms used in connection with polarized light must now be defined. In Fig. 2, let  $AO$  be the incident ray, striking the metallic surface at  $O$ .  $DO$  is the normal to the metallic surface at that point. Angle  $AOD$  is angle  $\theta$ , the angle of incidence. As the image of the source of light is formed on the metallic surface, and as the light from that source is plane polarized, the light striking the metal is plane polarized. The plane of the polarized light is represented by the vector  $PP'$ . The direction of this vector represents the plane of polarization of the light, and its length represents the amplitude of vibration. The angle made by this vector with the intersection of the plane of incidence (plane  $AOB$ ) and the metallic surface (the intersection is the line  $OB$ ) is the angle  $BOP$ , or angle  $\alpha$ , the azimuth angle.

This incident ray  $PP'$  may be split into two components, one lying in the plane of incidence  $CC'$  and the other perpendicular to it ( $EE'$ ). In the discussion that follows, these two components will be substituted for the ray, a procedure that is simplifying and accurate.

Two changes are possible during the reflection of this ray. Either of the components may suffer a change in amplitude, and one component may be retarded with respect to the other, creating a difference in phase between them.

First let us determine the effect of a difference in the change of amplitude of the two components on reflection, without any phase difference. The conditions are represented diagrammatically in Fig. 3.  $PP'$  is the incident

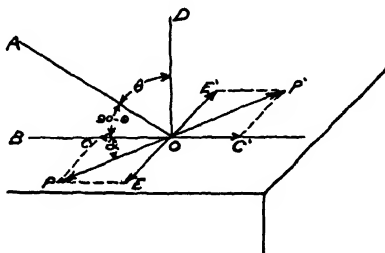


FIG. 2.

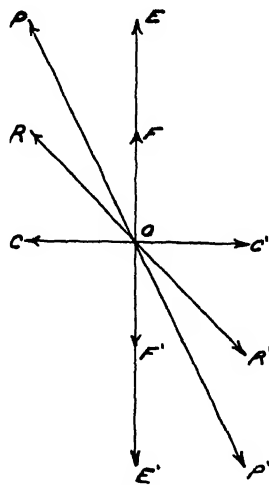


FIG. 3.

FIG. 2.—TERMINOLOGY INVOLVED IN STUDYING REFLECTION OF POLARIZED LIGHT.

FIG. 3.—ROTATION OF PLANE OF POLARIZATION DUE ONLY TO DIFFERENCE IN REFLECTIVITIES OF A SUBSTANCE FOR TWO COMPONENTS OF PLANE POLARIZED LIGHT.

ray,  $CC'$  and  $EE'$  are the parallel and perpendicular components. Let us suppose that  $CC'$  suffers no change in magnitude upon reflection, while  $EE'$  is reduced by one-half. Then  $EE'$  will become  $FF'$  after reflection, and the reflected ray (obtained by adding vectorially  $FF'$  and  $CC'$ ) will be  $RR'$ . Thus the plane of polarization is rotated by this reflection, but the resultant is still plane polarized light. Such a rotation occurs whenever the reflectivities of the metal for the two components differ.

The effect of a phase change alone is more difficult to picture. A new convention is necessary. A particle in the path of a light ray vibrates with a sine wave motion. If the light ray is plane polarized, these vibrations will lie in one plane, which we have called the "plane of polarization." A complete to-and-fro vibration of a particle in the path of the light ray will constitute an amount of time equal to the time required for the light to travel a distance of one wave length.

We can represent this vibration by the same vector  $PP'$ , which already indicates the plane of polarization and the amplitude of vibration. This convention is shown in *a*, Fig. 4. The vector  $PP'$  represents the vibration of a particle in the path of the light ray just before the light is

incident on the metal surface.  $O$  represents conditions at 0 time, 1 after one-quarter of a wave length, 2 after one-half wave length, and so on.

This vibration is separated into the two component vibrations, one parallel and one perpendicular to the plane of incidence. These are

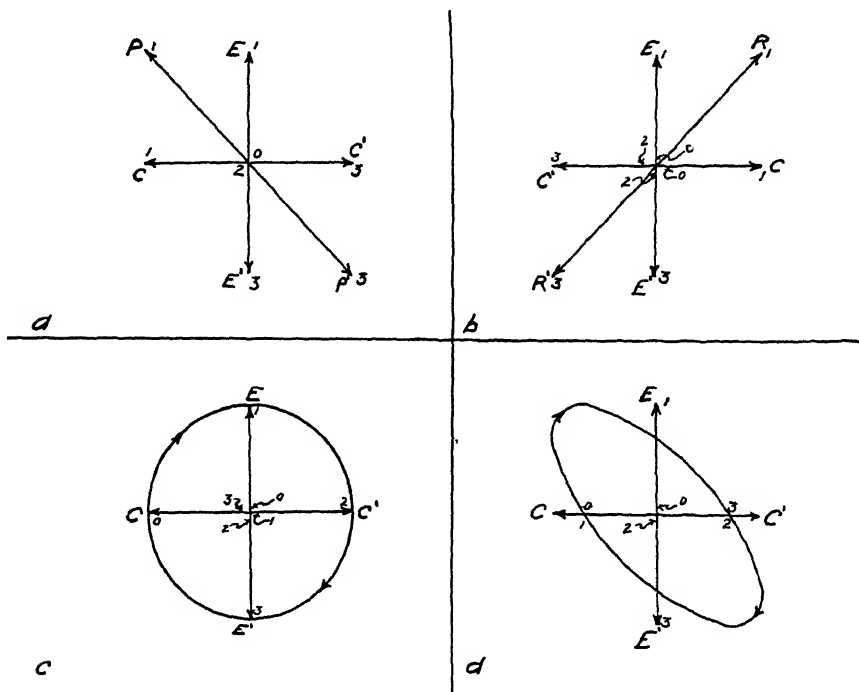


FIG. 4.—EFFECT OF VARIOUS PHASE DIFFERENCES ON KIND OF REFLECTED POLARIZED LIGHT WHEN INCIDENT RAY HAS AZIMUTH ANGLE OF  $45^\circ$ .

- Plane polarized incident light.
- Light plane polarized at angle of  $90^\circ$  to incident light produced by one-half wave-length phase difference.
- Circularly polarized light produced by one-quarter wave-length phase difference.
- Elliptically polarized light produced by one-eighth wave-length phase difference.

$CC'$  and  $EE'$ . We will assume imaginary vibrating particles in these components, whose positions at the times 0, 1, 2 and 3 are represented by those same figures.

To obtain the position of the particle vibrating in  $PP'$  at any time from the positions of the imaginary vibrating particles in the components, we add vectorially the distance of the particle  $CC'$  from its midpoint of travel at that time, to the distance of particle in  $DD'$  from its midpoint at that time. Repeating this for all times, we find the complete motion of the particle that represented by the vector  $PP'$ .

With this convention, it is possible to illustrate the effect of introducing a phase difference between the components. Let us suppose that

one of these components is retarded during reflection with respect to the other. Jamin<sup>(13)</sup> tells us that a ray polarized perpendicularly to the plane of incidence is always retarded with regard to a beam polarized parallel to the plane of incidence. In *b*, Fig. 4, we introduce a phase difference of one-half a wave length.  $CC'$  is the parallel component and  $EE'$  the perpendicular component.  $EE'$  is retarded with respect to  $CC'$ . Therefore, at the time 0, if we arbitrarily consider ray  $EE'$  to be as in *a*, at the time 0, the particle will be in the center moving upwards. The particle in component  $CC'$  will have gone on for half a wave length, and will now be in the center moving to the right, instead of to the left as in *a*. Taking the subsequent times 1, 2 and 3 at intervals of one-quarter of a wave length and summing the vectors at all times, the resultant is found to be light plane polarized and at an angle of twice the azimuth angle (in this case  $90^\circ$ ) to that of the incident ray, and with the same amplitude.

The effect of a quarter-wave phase difference is shown in *c*, Fig. 4. We proceed exactly as for *b*. When we sum the component vectors, the motion of the particle representing the resultant is seen to be a circle. The reflected light accordingly is called circularly polarized light.

Circularly and plane polarized light are special cases of the general results obtained by introducing a phase difference between the components of plane polarized light. The general case is that of elliptically polarized light. Such a case is shown in *d*, Fig. 4, where a phase difference of one-eighth wave length is introduced. The resultant vector traces an ellipse.

With an angle of azimuth of  $45^\circ$  (giving equal parallel and perpendicular components) as shown in Fig. 4, introducing increasing amounts of phase difference up to one-quarter wave length produces elliptically polarized light whose major axis is in the same direction as the plane of polarization. With phase differences above one-quarter wave length up to the maximum producible by metallic reflection (one-half wave length at  $0^\circ$  incidence), the major axis of the elliptically polarized light is at right angles to the plane of polarization of the incident ray. A phase difference of one quarter wave length produces circularly polarized light only when an azimuth angle of  $45^\circ$  is used.

If any other azimuth angle is used, the effect will be different. With increasing phase differences up to one-quarter wave length, the ellipticity will increase. The major axis of the ellipse will slowly rotate, until at a one-quarter wave-length phase difference the major axis of the resultant elliptically polarized light will be the greater component of the incident ray. Increasing the phase difference to one-half wave length will decrease the ellipticity of the polarized light, and will rotate the major axis to an equal angle on the other side of the greater component from the incident ray, and again produce plane polarized light.

Of all the types of polarized light, only one is capable of being entirely absorbed by the analyzer nicol. This is plane polarized light. To analyze circularly and elliptically polarized light, it is necessary to use some device such as a Soleil-Babinet compensator. This is an optical device so arranged that it can introduce any desired phase difference into polarized light. By means of this compensator, we may change polarized light with any amount of ellipticity to plane polarized light. With this compensator and a nicol prism, all elements of every type of polarized light can be determined.

It is possible by the use of these two devices to determine the change of amplitude of both components and the phase difference between them introduced by reflection.

Jamin<sup>(13)</sup> investigated the reflection of plane polarized light from several metals, including iron and zinc. His conclusions follow:

1.—Intensity changes—for steel and all metals investigated: (a) For the plane of polarization parallel to the plane of incidence and the angle of incidence decreasing from  $85^\circ$  to  $20^\circ$ , the intensity decreases regularly; (b) plane of polarization perpendicular to the plane of incidence, the angle of incidence decreasing from  $85^\circ$  to  $20^\circ$ , the intensity decreases to a minimum, varying for the metal, and then increases again, usually to higher values than at high angles of incidence.

2.—Phase differences: (a) A ray polarized perpendicular to the plane of incidence is always retarded with respect to a beam in  $0^\circ$  azimuth; (b) phase difference is nil at  $0^\circ$  incidence, increasing progressively until the angle of incidence is  $90^\circ$ , where the change of phase is one-half wave length and having the value of one-quarter of a wave length at the angle of maximum polarization.

Some of Jamin's data for iron are shown in Fig. 5. These results are for only one type of light. The values will vary with the color of light used. Jamin also gives data on the phase differences produced by zinc at different angles of incidence. The data are not reproduced because they closely resemble the data for iron. Jamin's data show that the general effect obtained is not alone a rotation of the plane of polarization or the formation of elliptically polarized light, but a combination of the two.

Wood<sup>(10)</sup> says that according to the electromagnetic theory of light there should be a sudden change of phase on passage through the polarizing angle, and that plane polarized light should be reflected as plane polarized light. Actually, this is not true, as the typical data in Fig. 5 show. Theory has been more closely approached in freshly prepared surfaces. Experiments indicate that the disagreement with the theory is caused by a surface film having optical properties different from the body of the substance. To check with this, Drude<sup>(11)</sup> has found that freshly cleaved crystal surfaces showed almost no traces of elliptical



polarization, and that the elliptic polarization appeared after the surface was exposed to air for some time. Wood suggests that this would be particularly true in regard to metals, and says that it is very difficult to be certain that no surface films are present. He suggests also that in metals a freshly cleaved surface would be free of them.

Wright<sup>(3,4)</sup> also mentions the effect of surface films. He says:

The general equations state that in case the azimuth of the plane of polarization of the incident wave is 0 or 90 degrees, the reflected beam is still plane-polarized; practical experience with such reflectors shows, however, that the reflected beam always reveals traces of elliptical polarization, even when the plane of polarization is horizontal or vertical. This is no doubt due, in the case of reflecting glass surfaces, to internal reflections; with a blank metal reflecting surface, such as the fresh silver side of a silvered mirror, it may result from strains in the outer film. Be the cause what it may, in no experiment was the elliptic polarization entirely removed and the accuracy of the settings was correspondingly diminished. Experience with the different types of reflectors did not demonstrate marked superiority of any one particular type. It is, of course, essential that the plane of polarization of the incident beam be strictly horizontal or vertical to reduce the amount of elliptic polarization present to a minimum.

In setting up the microscope for use with polarized light, this last mentioned precaution should be noted. The plane of polarization must be made parallel or perpendicular to the axis of the microscope (the center line drawn through the objective, vertical illuminator, and Stellite mirror; see Fig. 1) to obtain as dark a field as possible under crossed nicols.

Other complications are introduced by the microscope. When the microscope objective focuses the illuminating beam on the metal surface, the plane polarized light will be striking the metal surface with all angles of azimuth and all angles of incidence that the numerical aperture of the objective will permit it to transmit. The light reflected from the metal therefore will be plane and elliptically polarized light of varying degrees of ellipticity. The reflected beam will be nonuniform in composition, and the higher aperture objectives will contain the greatest ellipticity of light, and therefore the lightest field under crossed nicols.

There is one final cause of the degeneracy of the plane polarized light. To have only light polarized in a single plane obtained from a nicol prism, the light passing through it must be a parallel beam. Fig. 1 indicates that in the metallograph used this condition is not fulfilled in either the polarizing or analyzing nicol. If space were available in the microscope, the illuminating beam passing through the polarizing nicol should be made parallel by a divergent lens and reconverged after it has passed through the nicol. In addition, the analyzer used should be ahead of the eyepiece in the optical system, so that the rays are less divergent when they pass through the nicols. Unfortunately, with the ordinary objectives, the regular type of analyzer at this point causes an astigmatic image to

be formed. This is so because rays that make up one point of the image are passing through the analyzer at different angles and so pass through

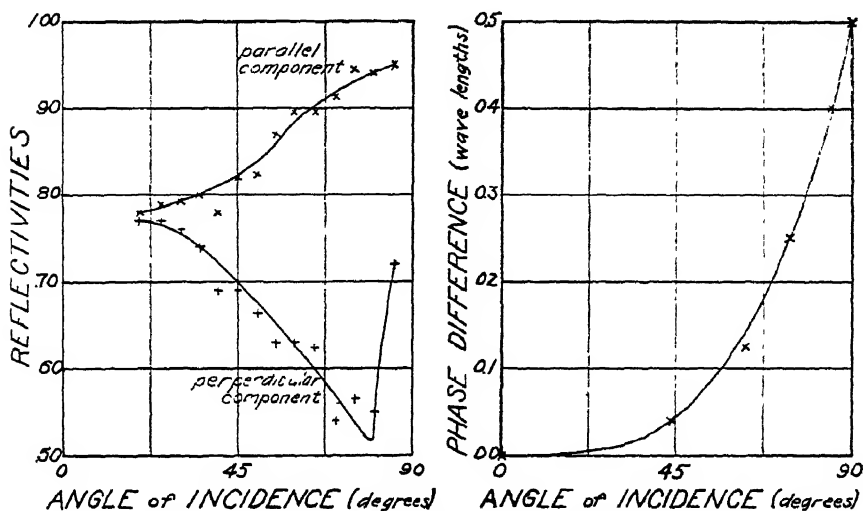


FIG. 5.—OPTICAL CONSTANTS (REFLECTIVITIES AND PHASE DIFFERENCES) OF IRON FOR VARYING ANGLES OF INCIDENCE ACCORDING TO JAMIN. VALUES WERE OBTAINED USING DEEP RED LIGHT.

different amounts of the material of which it is made. For this reason, the ordinary type of cap analyzer is used, because this does not form an astigmatic image.

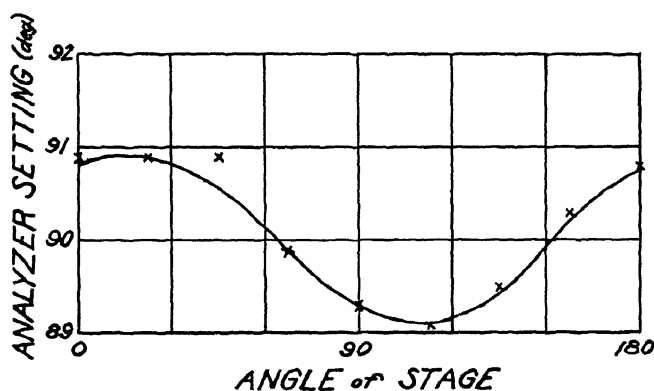


FIG. 6.—VARIATION OF PLANE OF POLARIZATION OF LIGHT REFLECTED FROM TIN CRYSTAL OF WHICH ORIENTATION IS VARIED BY ROTATING STAGE.

The orientation of the face of the crystal exposed was not determined. Light of approximately 5300 Å. wave length was used.

The ideal arrangement of the optical system would be to employ some of the new objectives that are corrected for a tube length of infinity. This means that rays from the different parts of the objective back lens

which form any particular point of the image are parallel to each other. Accordingly, they all pass through the nicol at the same angle and all have the same plane of polarization. Therefore, when the image is focused, each point in it has a definite plane of polarization, although this plane may differ in various points of the image. This same reasoning can be applied to the illuminating beam.

### EFFECTS OF ANISOTROPY

One of the features of this instrument is that it can distinguish anisotropy. (Anisotropy means having different physical properties in different directions, in this case the optical properties are the ones implied.) If the coefficient of reflection or the phase differences produced by a substance are different in different directions, the instrument can determine the fact. Schwarz<sup>(5)</sup> says:

... the most important result received by the employment of polarized light is the fact that isotropic substances may be held apart from anisotropic due to the fact that only slides of isotropic substances remain dark in any position when being examined under crossed nicols.

He says that all others rotate the plane of polarization, forming the various colors of polarization upon rotation of the metal slide. With few exceptions, according to Farnham,<sup>(12)</sup> isometric substances are isotropic, and all other crystallized minerals are anisotropic. (An isometric substance is one that is crystallographically developed alike in three directions at right angles to each other.)

To test the functioning of the instrument, an anisometric metal zinc, crystallizing hexagonally, was chosen to see whether anisotropy could be determined in the polarization microscope. A sample of electrolytic zinc was prepared as a metallographic specimen. It was examined under unpolarized light in a microscope, and was found to have only the ordinary appearance of a polished metal, showing no traces of individual crystals. It was then examined under polarized light with crossed nicols. The various crystals of the metal could then easily be differentiated from one another by considerable differences in intensity, some crystals being as dark as any isotropic metal under crossed nicols, while others were in varying shades of brightness. A photomicrograph is shown in Fig. 7. (The many scratches in this picture were scarcely noticeable under ordinary illumination. Any roughening of the surface of a specimen is very apparent under crossed nicols.) This effect has been reported by other investigators, but no discussion of its cause was recorded. For this reason, additional experiments were performed. The iris diaphragm (Fig. 1) was stopped down to the smallest opening obtainable, which was less than 1 mm. This produces a beam of light illuminating the metal specimen at practically perpendicular incidence. The contrast

of one grain to another appeared to increase during this experiment. It was noticed also that the lower the numerical aperture of the objective, the greater the contrast. These two experiments show that whatever factor was causing one grain to appear lighter than another was operating at an angle of incidence of  $0^\circ$ .

One further experiment was tried: If the lightness is caused by a rotation of the plane of polarization, each grain should be darkened at some position of the analyzer. Accordingly, the analyzer was rotated from one side of the crossed position to the other. If one crystal of the metal was darker than another, it remained so in any position of the analyzer, although the intensity of light from them naturally did vary. When the metal slide was rotated through one revolution, each crystal alternately lightened and darkened four times. This proves that the contrast is caused by the formation of elliptically polarized light in amounts depending on the orientation of the crystal, and not by a rotation of the plane of polarization.

It is then apparent that, even at perpendicular incidence, a zinc crystal can introduce a phase difference into plane polarized light, the magnitude of the phase difference depending on the orientation of the zinc crystal. This is contrary to the theory as given by Wood,<sup>(10)</sup> and to the experimental evidence of Jamin.<sup>(13)</sup> For this reason, an attempt at an explanation reconciling the two sets of evidence was made.

It was thought that the so-called etching effect that Sachs<sup>(14)</sup> first mentions might have some connection with this case. Primrose<sup>(6)</sup> also mentions this phenomenon, which depends on the fact that when a metal specimen is etched numerous small pits are formed in the surface of most crystals. The polarized light may be reflected from these pits back into the objective. If it is, it suffers reflection at large angles, which creates a considerable phase difference if the ray has an azimuth angle differing much from  $0^\circ$  or  $90^\circ$ , since any metal introduces a phase difference at other than zero degrees incidence. This explains why some crystals are dark and others light when a heavily etched specimen of an isotropic metal is observed under polarized light. Those in which the sides of the pits were parallel or perpendicular to the plane of polarization would be dark. All others would be in varying shades of lightness, depending on azimuth angle. The result of any slight roughening of the surface is noted in Fig. 7, where scratches that are not noticeable under ordinary light become extremely distinct with crossed nicols.

It seemed that this effect possibly would offer an explanation in the case of zinc. Of course, the piece of zinc used was a polished specimen, but zinc recrystallizes at about room temperature and it was thought that recrystallization might have an effect similar to that of etching, at least in so far as the production of pits was concerned. When the polished piece of zinc was held at a favorable angle to the light, the crystals could be seen with the naked eye, greatly resembling an etched surface.

If this were the reason for the anisotropy of zinc, an anisometric metal, there is no reason why a recrystallized piece of an isometric metal should not be similarly anisotropic. A polished piece of nickel was heated for short times at temperatures varying from  $300^{\circ}$  to  $500^{\circ}$  C. in very pure hydrogen. After the heating to the highest temperature the boundaries of the crystals could be seen, showing that recrystallization had occurred, but no heating temperature made the nickel anisotropic. To see whether the temperature of heating had some effect on the recrystallization, so that it proceeded in a different manner, a polished



FIG. 7.—POLISHED SAMPLE OF ZINC AS SEEN UNDER POLARIZED LIGHT WITH CROSSED NICOLS.  $\times 50$ .

Individual crystals can be seen here, while ordinary light shows only a polished surface. Needles in crystals are attributed to a recrystallized worked surface layer. Scratches, so noticeable here, are barely discernable by ordinary illumination, illustrating effect produced by polarized light with slight roughening of surface.

piece of zinc was heated in hydrogen to as high a temperature as possible below melting, to see whether this destroyed the anisotropy of the zinc. The heating made the grain boundaries visible under ordinary light, as seen in Fig. 8, but did not destroy the anisotropy, as seen in Figure 9. Here again scratches unseen in ordinary light became very distinct with crossed nicols.

These experiments seem to show that zinc produces a phase difference when reflecting polarized light perpendicular to the plane of the sample. Although this is not in accord with Jamin's work, he used a polycrystalline sample and thus obtained an average effect. In addition, the effect may have been too small to be detected. Wright<sup>(34)</sup> substantiates the latter view, saying that in general the phase difference produced by reflection even from a highly birefringent (or doubly refracting) substance is very small.

Several other anisometric metals were examined—magnesium, bismuth, antimony, titanium (which crystallize in the hexagonal system) and tin (which crystallizes in the tetragonal system). The crystals of all but titanium showed differences in contrast under crossed nicols. The hexagonally crystallizing metals appear to have the same effect as zinc, that of the production of elliptically polarized light at  $0^\circ$  incidence.

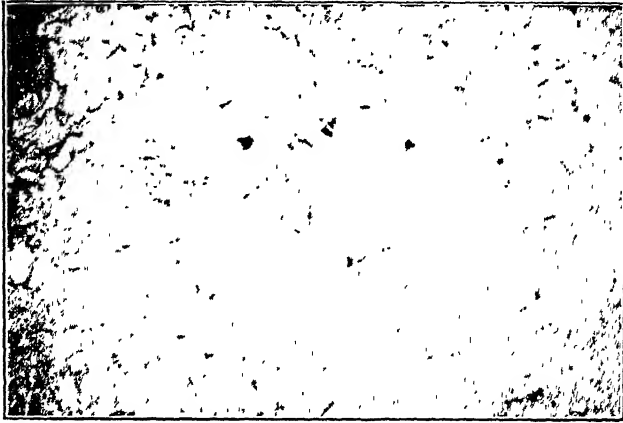


FIG. 8.—ZINC RECRYSTALLIZED AT  $350^\circ\text{C}$ . IN HYDROGEN AS SEEN BY ORDINARY ILLUMINATION.  $\times 50$ .



FIG. 9.—SAME FIELD AS FIG. 8 SEEN BY POLARIZED LIGHT, CROSSED NICOLS.  $\times 50$ . Crystals now have considerable differences in contrast due to varying orientation. Scratches hardly noticeable by ordinary light are very distinct by polarized light.

Tin, crystallizing tetragonally, has the effect of rotating the plane of the polarized light. For every crystal in the metal there is some setting of the analyzer, which causes darkening of that grain. The setting is different for different ones and some may rotate the plane of polarization clockwise and others counterclockwise. Setting the analyzer first slightly on one side of the crossed position and then slightly on the other

causes a reversal in the contrast of the grains. This effect is illustrated in Figs. 10 and 11. The magnitude of the rotational effect was investigated. The microscope was focused on one particular grain, and as the stage was rotated the plane of polarization was determined. The graph of analyzer setting against stage position is shown in Fig. 6. For this determination, approximately monochromatic light of the wave length

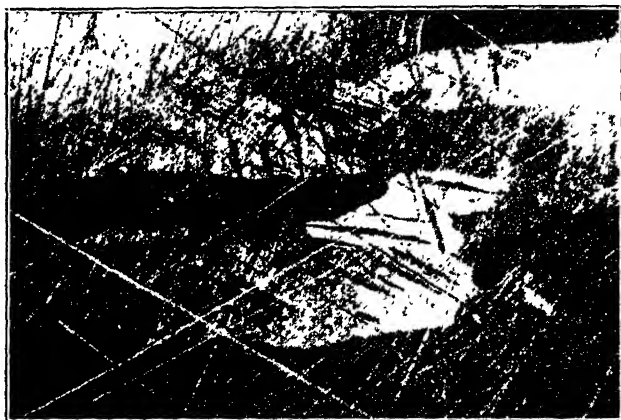


FIG. 10.—PURE TIN AS POLISHED, SEEN BY POLARIZED LIGHT WITH ANALYZER SLIGHTLY COUNTERCLOCKWISE OF CROSSED NICOLS POSITION.  $\times 50$ .



FIG. 11.—SAME FIELD AS FIG. 10, SEEN BY POLARIZED LIGHT WITH ANALYZER SLIGHTLY CLOCKWISE OF THE CROSSED NICOLS POSITION.  $\times 50$ .

Note reversal in intensities of individual crystals from those in preceding photomicrograph.

of the green mercury line was used, and the iris diaphragm was stopped down to give perpendicular incidence.

All anisometric metals examined except titanium have exhibited anisotropy. Later it was found that some inclusions such as nitrides and carbides also lacked detectable anisotropy. The reason they do not

exhibit anisotropy may be due either to the smallness of the effect obtained or to the presence of a surface film generated during the preparation of the sample. Such a surface film has lost the directional properties of the underlying metal, and probably is composed of crystallites with random orientations. It could not be anisotropic. To make possible the observation of differences in crystals under polarized light, this film must be removed. Two methods suggest themselves: The first, etching, would be inconclusive because of the possibility of an etching effect, already mentioned. The second, heating to recrystallization, has been proved to be satisfactory. This method has also been suggested by Hanstock.<sup>(15)</sup>

Therefore the titanium was heated to 800° C. in hydrogen. Apparently the gas was not dry enough, because surface oxidation resulted. The titanium afterwards appeared anisotropic, but the results cannot be considered definite because of the oxidation.

There is further evidence to show that surface films are produced during polishing. In Fig. 7 will be noticed a number of needles inside each zinc crystal. This specimen was then polished carefully for a long time, after which the needles were mostly polished away and only the crystals remained. The needles were present only in a surface layer, which must have been an amorphous layer, produced during polishing. Because of the low recrystallization temperature of zinc, this layer did not remain amorphous and grain growth proceeded. Some of the large crystals lying under the film absorbed the overlying metal except where needles had grown so favorably oriented that the large grains did not absorb them. A short polishing gave the result in Fig. 7. Long-continued polishing will remove the surface layer containing the needles and only the crystals will remain. Such a film may have formed on the titanium and did not recrystallize. These two instances show that surface films are likely to conceal the possible anisotropy of a substance; the film must be removed before definite conclusions can be drawn. Even then, the effects may be of too small a magnitude to be observed, inasmuch as all anisotropic effects obtained by reflected light studies are much smaller than those obtained in studies by transmitted light.

#### EFFECTS OF STRESS

Two particular cases of the effects of stress as seen microscopically under polarized light will be considered: (1) The metal is stressed below the elastic limit and is being examined while under that stress; (2) the metal is stressed beyond the elastic limit and is examined after the stress has been removed. The first of these has an analogy in the study of transparent objects under polarized light. The study there is called photoelasticity. Use is made of the fact that stress changes an isotropic substance to an anisotropic one and an anisotropic material introduces phase differences into polarized light. The same basic



principle may be applied to the study of metals. Stress introduces directional properties into isometric metals, which may make them sufficiently anisotropic to be detected by the polarization microscope. Undoubtedly the effects are minute, even more so than the slight ones observed with anisometric metals.

This problem may be attacked using either low or high magnifications. At low powers, perhaps from one to ten diameters, the stress variations in different parts of the sample could best be determined. This method probably offers the greatest chances for success, as it eliminates the difficulties present when higher magnifications are used. With the latter, the iris diaphragm must be stopped down to a very small opening to obtain a dark field with crossed nicols. This naturally destroys the resolving power of the instrument, and we must be content either with low resolving powers or a light field of view. The use of low magnifications eliminates the many difficulties arising when high powers are used. Unfortunately, the instrument used did not have facilities for using low powers.

At low magnification, the stress will vary fairly uniformly from point to point. According to the mosaic theory, this will not be so at high magnifications. This mosaic theory is based on the tenet that crystalline materials are composed of blocks of a number of atoms, crystals being made up of such blocks. The theory explains a number of hitherto unexplainable points in the structure of metals and probably it is at least partly true. If it is true, the effect of having a material in unit blocks will be to create regularly spaced nonuniformities in the surface. When the material is stressed, these nonuniformities will be most stressed and it will exhibit the greatest anisotropy at these points. Observation at high powers under the polarization microscope should reveal a network structure corresponding to these most stressed portions which are alleged to be the future slip lines.

An attempt was made to observe this effect. A press was mounted on the microscope stage and the metals squeezed in it. Due perhaps to the extreme lightness of the field with oil-immersion objectives, no anisotropic effects were observed. The experimental difficulties to be overcome here are great, and must be overcome to obtain definite results. This field is one of great importance, especially as a source of the confirmation of the mosaic theory. No observations of any such effects have as yet been published.

When the metal has been stressed beyond the elastic limit and therefore is in a state of permanent strain, this deformation is detectable for another reason and depends upon a secondary effect, the previously mentioned "etching effect," for its observation. Deformation of a metal produces along slip lines a number of small crystallites of jumbled orientations. If the specimen is isometric, examination of a polished

specimen will not disclose this condition, but if the slide is etched, the metal will etch differently in the deformed portions and polarized light will reveal that fact. This effect has been found. Schwarz and Ahmad<sup>(16)</sup> have observed qualitatively the presence of deformation in a specimen of pearlite. They also say that the sample must be etched to observe the strain.

The probability of detecting elastic stress in metals by the use of this instrument is very small. Even with very anisometric substances, rotations of the plane of polarization amount to only a degree or so. Where only the small amount of anisotropy due to elastic stress is present, the effects will probably be too small to be detected, at least until instruments much more sensitive than those now in use are developed.

#### IDENTIFICATION OF INCLUSIONS

If an inclusion is an anisometric substance and exhibits anisotropic surface effects, that fact may be evident under the polarization micro-

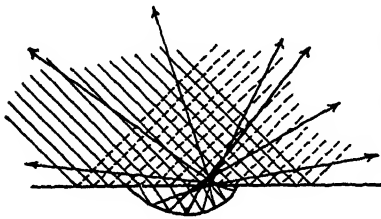


FIG. 12.

FIG. 12.—SCATTERING OF BEAM OF LIGHT BY TRANSPARENT INCLUSION IN SURFACE OF METAL SPECIMEN.



FIG. 13.

FIG. 13.—DIAPHRAGM HELPFUL IN OBTAINING CONTRAST IN STUDY OF TRANSPARENT INCLUSIONS.

scope. This anisotropy may be obscured at times even when it is present, by the greater intensity of light arising from the transparency of the inclusion. A better understanding of the mechanism of the latter effect can be obtained by a study of Fig. 12 which shows a cross section of a polished metal surface with a transparent inclusion in the surface. A single beam of plane polarized light from the microscope objective, represented by the light solid lines, is incident from the left. The surface reflected light is shown by the dotted lines. This light is either plane or elliptically polarized. The greater part of it is removed by the analyzer in the crossed nicols position, because of the generally small ellipticity of the light. A portion of the light incident on the surface of the inclusion is refracted into it and transmitted through it. It is reflected from the metal-inclusion interface, then transmitted and refracted out of the inclusion as indicated by the heavy lines.

These rays coming out of the inclusion no longer are plane polarized, as they were before entering the inclusion. Random reflections from the metal-inclusion interface, and the possible double refraction of the substance of the inclusion, assist in changing the original plane polarized light so much that it can be considered depolarized.

If this specimen is viewed with parallel nicols, the ordinary microscopic appearance of the inclusion by reflected light is obtained. The intensity of the light reflected from the surface of the inclusion is so great that the much weaker transmitted light cannot be seen. If the majority of this surface reflected light is removed by crossing of the analyzer nicol, the transmitted light acquires a greater relative intensity, and if the inclusion is sufficiently transparent its transmitted color can be detected. Any other means of removing the surface reflected light will serve as well. For instance, a dark field illuminator in which the surface reflected light is outside the cone of rays transmitted by the objective also shows the transmitted color of an inclusion. Where an inclusion is not transparent, the polarization microscope may be more helpful in the identification by determining the presence of anisotropic surface effects of sufficient magnitude. Effects due to inclusions described by other investigators have always been due to the transparency of the inclusion. In this work use was made of the fact that the polarization microscope can also detect surface anisotropy.

In Fig. 12, in the particular shape of inclusion shown, which is a rather common one, since many inclusions have a rounded external form, the light coming from the interior of the inclusion is refracted over  $180^\circ$ , though it is illuminated by a beam of light with a single angle of incidence. This scattering effect is similar for a beam with any angle of incidence. An objective of high numerical aperture will gather more of these scattered rays, and with such an objective any particular inclusion should appear brighter than with one of lower numerical aperture. On investigation, this effect was noted. Thus with inclusions that are only slightly transparent, an objective of higher power may help in its identification.

To obtain the greatest possible brightness of the inclusion relative to the body of the metal, only plane polarized light should be reflected from the surface. To obtain this result, we must eliminate the rays that have a large angle of incidence and at the same time an azimuth angle differing much from zero, or  $90^\circ$ . A diaphragm was therefore constructed to control these angles. It was designed from Jamin's data for steel, to be placed adjacent to the iris diaphragm at 4, Fig. 1. In use, there should not be more than 0.25 per cent of the total illumination left after the nicols are crossed. An enlarged view of the diaphragm is shown in Fig. 13. In use one of the axes is placed parallel to the plane of polarization. This diaphragm was used in all pictures taken of inclusions.

A transparent doubly refracting (birefringent) substance can produce anisotropic effects in two ways. One of these is by reflection, and the manner of it has been discussed. The effect obtained depends on two factors, the intensity of the double refraction of the substance and the orientation of the lattice. The other is by transmission, and cannot be observed in ordinary inclusions. Only ideally shaped inclusions can produce such an effect. The anisotropic effect obtained by transmission in a doubly refracting substance depends on three factors, the two previously mentioned for reflection, and the amount of material traversed by the ray. In Fig. 12 it can be seen that of the many rays traversing the specimen no two travel the same distance through the inclusion, even with a single angle of incidence. Employing all angles of incidence and azimuth, no ordered effect can result. The only result can be a practical depolarization of the light.

Accordingly an inclusion can exhibit two effects; a color due to light transmitted by it and an interference color due to anisotropic effects in surface reflection. If both are present, the one that has the greatest intensity will predominate, generally to the practical elimination of the other, and will be the one observed in the microscope.

If an inclusion is observed to have a certain color and there is doubt as to which of these two effects it is due, we have only to rotate the microscope stage to decide. If the color is that due to an anisotropic effect on reflection its intensity will vary with the orientation. If the transmitted color of the inclusion is being observed, the rotation will not affect it.

A number of inclusions were examined, to illustrate the variety of effects obtainable, so that other investigators may be aided by a knowledge of the features to be looked for in such identification. Much careful study must be spent on inclusions in each metal before standards of identification can be set up, particularly in regard to inclusions in iron and steel. No such attempt was made in their investigation, but several examples of typical effects produced by inclusions and a short description of each are in the following pages.

### *Cupron Rectifier*

Cuprous oxide is a deep ruby red by transmitted light and a bluish gray by reflected light. Inclusions of cuprous oxide in copper show the transmitted color under crossed nicols. This effect has been observed by several investigators, notably Schwarz,<sup>(6)</sup> who shows a photomicrograph in natural colors. He recommends the use of the polarization microscope to distinguish between oxide and sulfide in copper. Both oxide and sulfide have the same appearance by reflected light, but the sulfide is not transparent and observation under crossed nicols reveals

this fact by showing the inclusions of sulfide to be dark, while the oxide shows its characteristic red color.

A cupron rectifier is made of a number of copper plates whose surface has been oxidized in such a way as to form a layer of cuprous oxide. One of these plates was mounted in bakelite and prepared for microscopic examination. During mounting, the brittle oxide layer was cracked in several places, one of which is shown in the photomicrograph by ordinary light (Fig. 14). Small globules of cuprous oxide can be seen in the copper metal in the upper portion of the photograph.

The cracking of the oxide layer proved to be a fortunate occurrence, because when the sample was examined under crossed nicols only the

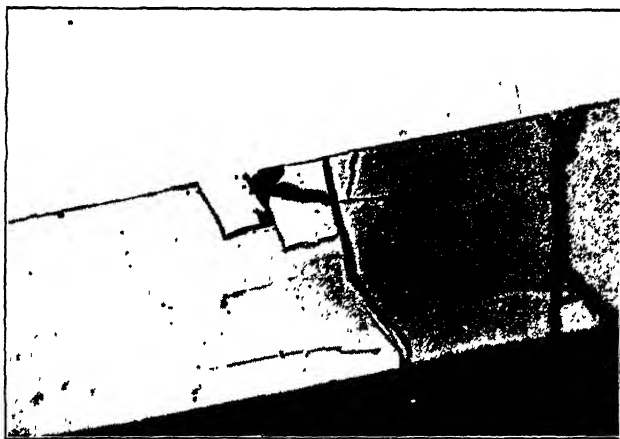


FIG. 14.—SECTION OF EDGE OF CUPRON RECTIFIER SEEN BY ORDINARY ILLUMINATION.  $\times 250$ .

Upper part is copper backing, small cuprous oxide inclusions may be seen. Lower part is cracked portion of cuprous oxide coating. Seen by ordinary light, the cuprous oxide is a bluish gray.

parts that were in fragments showed the transmitted color of cuprous oxide. All other places were dark. The cracks in the oxide formed surfaces upon which back reflections can take place and, thus, light transmitted by the oxide of the coating could be carried back into the objective and be seen through the microscope. Without these internal reflections the light would go down through the oxide until it all was absorbed. Three places where internal reflections can be seen (the brighter ones) in the oxide coating are in Fig. 15. (The red appears white, as the picture was taken on a panchromatic plate.) In this same photograph the cuprous oxide in the copper also displays its characteristic red color. The color is very bright, as the whiteness of the inclusions illustrates.

Close observation of the oxide inclusions as seen under crossed nicols reveals an interesting phenomenon. In most of the inclusions a dark cross can be seen. Some inclusions show in addition a number of

concentric circles, but these are not apparent in Fig. 15. The cross and circles have an appearance strikingly similar to that of some interference figures which are observed under a high-power petrographic microscope. However, the causes of its formation here are so different and the phenomena so general that the causes and mechanism of its appearance will be discussed in detail at the end of this section.

Fig. 15 reveals another interesting phenomenon. The oxide coating is seen to be composed of four different crystals, which appear with slightly different intensities. One is on both of the central fissures in the oxide; the one to the left extends out of the photomicrograph, the one directly at the right extends slightly beyond the next fissure,

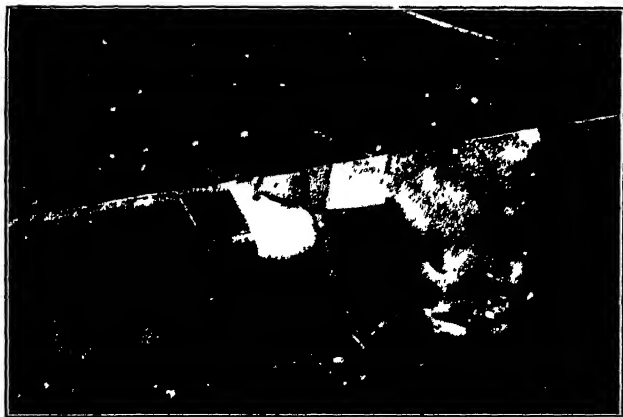


FIG. 15.—SAME FIELD AS FIG. 14, SEEN BY POLARIZED LIGHT, CROSSED NICOLS.  $\times 250$ .

Cuprous oxide inclusions now appear deep red (shown here as white) as do two cracked portions of oxide layer. This is transmitted color of cuprous oxide. Rest of cuprous oxide coating can be seen to be composed of individual crystals, which appear in polarization colors, deep blues and greens.

and the last one is beyond that. These differences in contrast are due to a surface polarization effect—no sign of these individual crystals can be seen in the photomicrograph by ordinary light.

The differences in these crystals are much more apparent in natural colors. The crystals are deep blues or purples and greens. Turning the analyzer from one side of the crossed position to the other reverses the hue of the crystals. Rotation of the stage causes a change in shade.

It has been said before that the amount of rotation or phase difference suffered by the plane polarized light varies for the different colors. For a substance that rotates the plane of polarization the analyzer can be set at the crossed position for any one color, thus eliminating it from the reflected light. The color seen will vary with the setting of the analyzer. For a substance that produces a phase difference, thus reflecting elliptically polarized light, the different colors will have different ellipticities. By crossing the nicols, varying amounts of each color can be retained.

The color that predominates is the one with the greatest ellipticity. The color is not changed in hue by rotation of the nicols.

It is thus apparent that the surface anisotropy of the cuprous oxide is due to a rotation of the plane of polarization rather than to the formation of elliptically polarized light.

Ordinary cuprous oxide inclusions in copper must exhibit the same surface anisotropy that this larger mass does. Cuprous oxide inclusions in copper are then an example of a substance exhibiting an anisotropic effect which is obscured by the much greater intensity of light arising from the transparency of the inclusions.

These results bring forth an apparent inconsistency. Cuprous oxide is by transmitted light an isotropic substance, yet by reflected light is anisotropic. It does not seem that one substance could have such divergent properties, but there is an explanation that is very plausible.

It is known that cuprous oxide in the presence of air will form a surface layer of cupric oxide, which is anisotropic. Such a film would probably have a definite orientation with respect to the underlying cuprous oxide and the crystalline surface of cupric oxide will be a replica of the underlying crystals of cuprous oxide. This surface will be anisotropic and could then produce the particular effect that was observed.

For this reason, surface anisotropy is not an unqualified indication that the substance is anisotropic. The possibility of the presence of a surface film should always be taken into account.

### *Chromium Inclusions*

A dozen samples of chromium with varying compositions were examined under both the ordinary and polarization microscopes. Many inclusions were present in each sample. In all of these, as viewed by ordinary light, only two general kinds of constituents could be seen. One of these was light gray in color. It sometimes occurred alone; usually angular in external form. As viewed by this polarization microscope it was not transparent. This constituent at other times was present as a eutectic with a dark gray constituent, which never occurred alone. This eutectic combination was transparent and under crossed nicols was found to have all variations of color between orange, brown and green. The green color closely resembled that of green chromium oxide, but its composition was not known. Photomicrographs of a sample of chromium containing this eutectic are shown in Figs. 16 and 17. In the latter, the natural colors of the inclusions are as follows: The left-hand inclusion is green, the round one next is a very bright orange, and the last two are both orange with enough brown to dull its brilliance.

A sample of very pure electrolytic chromium was then melted in an alundum crucible in an Arsem vacuum furnace under a pressure of less than 1 mm. A slight amount of oxide was present on the surface of

each piece of chromium. By ordinary light this sample showed the same two general constituents as a eutectic as the commercial varieties, but under polarized light showed only the colors green and orange. Photomicrographs of some of the inclusions in the sample are shown in Figs. 18 and 19. In the latter, the upper large inclusion is green and the lower

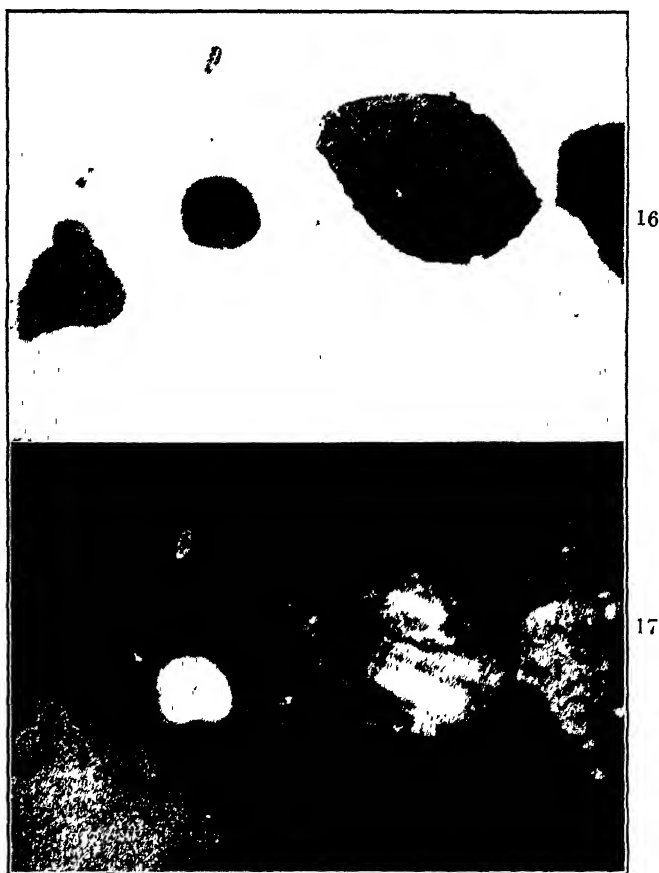


FIG. 16.—INCLUSIONS IN COMMERCIAL CHROMIUM SEEN BY ORDINARY LIGHT.  $\times 250$ .  
FIG. 17.—SAME FIELD AS FIG. 16 SEEN BY POLARIZED LIGHT WITH CROSSED NICOLS.  
 $\times 250$ .

Inclusions are transparent and appear in their transmitted colors, which are varying shades of orange to brown, and green.

one is orange. Most of the small ones are orange. This sample of chromium was analyzed for silicon, but none was detected by the analysis.

The inclusions in a sample of chromium which contained only the light gray type were analyzed, and were found to contain a large amount of chromium and manganese, with very little iron and silica. Inclusions of this type were separated from the metal. They were examined by transmitted light in an ordinary microscope, and were found to be of



two types—one red and one green. They were therefore transparent, but evidently not in such amounts that their colors could be seen by this metallurgical polarization microscope. The same colors in similar inclusions were also found by the later work of Baeyertz,<sup>(9)</sup> who was able to determine their colors by the polarization microscope. His success

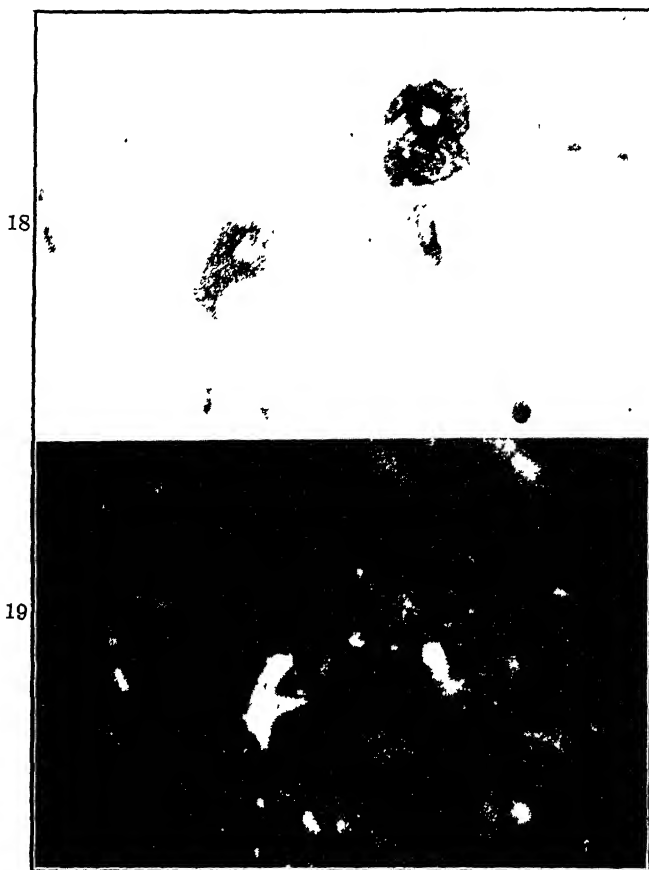


FIG. 18.—INCLUSIONS IN PURE ELECTROLYTIC CHROMIUM REMELTED WITH OXIDE AS SEEN BY ORDINARY LIGHT.  $\times 350$ .

FIG. 19.—SAME FIELD AS FIG. 18 SEEN BY POLARIZED LIGHT, CROSSED NICOLS.  $\times 350$ . Transmitted colors of these inclusions are either orange or green; the colors are brighter than in Fig. 17.

may be due either to the use of a microscope that gave a more completely dark field, or it may be that the difference in composition of his metal gave inclusions that were more transparent.

#### *Ferrous Oxide-ferrous Sulfide Inclusions*

A sample of hydrogen-reduced iron with 1 per cent each of ferrous oxide and ferrous sulfide added was melted in an Arsem vacuum furnace.

The duplex inclusions formed are seen in Figs. 20, 21 and 22. They are a eutectic of the two additions. Their identity was checked by the Campbell and Comstock method for the identification of inclusions in iron and steel as given on page 636 of the 1933 edition of the National

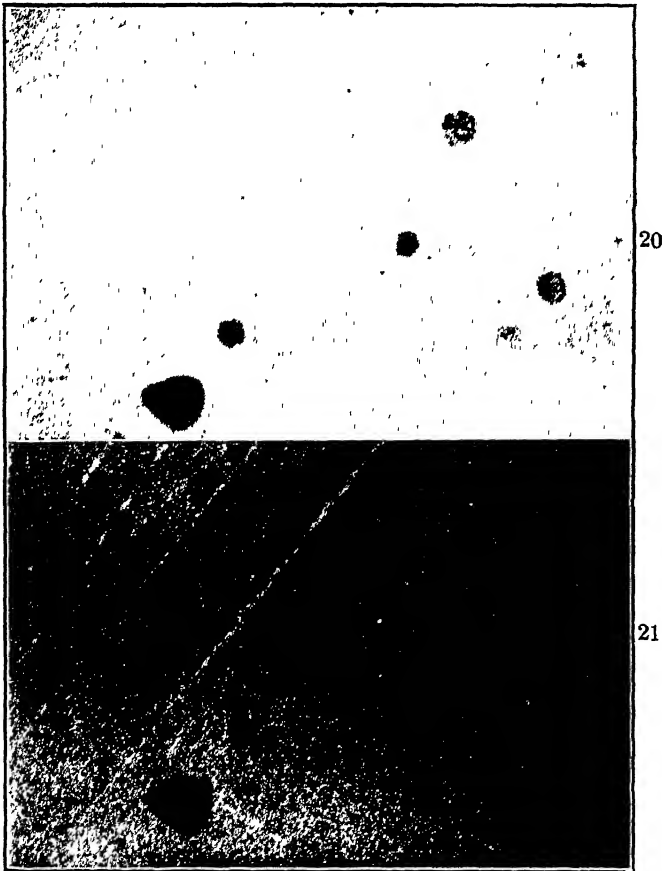


FIG. 20.—FeO (DARK)-FeS (LIGHT) EUTECTIC IN VERY PURE IRON SEEN BY ORDINARY ILLUMINATION.  $\times 350$ .

FIG. 21.—SAME FIELD AS IN FIG. 20 AS SEEN BY POLARIZED LIGHT WITH CROSSED NICOLS.  $\times 350$ .

Note FeS part of eutectic in upper inclusion. It now is lighter than the metal; in preceding photomicrograph it was darker. This proves that it is either transparent or anisotropic.

Metals Handbook. The ferrous oxide part of these inclusions is dark, the ferrous sulfide part is light. The inclusions are not transparent enough to be detectable. The ferrous sulfide exhibits decided anisotropy. The effect it produces is that of rotation of the plane of polarization.

The appearance of the inclusions with ordinary light is shown in Fig. 20. Attention must be focused on a particular inclusion to observe

this effect. The inclusion chosen is the one that appears at the upper right side of the photomicrograph. In this picture the ferrous sulfide is slightly darker than the background of metal, which means that its reflectivity is less than that of the metal. Using polarized light and rotating the analyzer exactly to the crossed position produces the appearance of Fig. 21. The ferrous sulfide in the inclusion now is lighter than the metal. The reflectivity cannot vary, so the only explanation can be that the ferrous sulfide is changing the polarized light more by reflection than the metal is. If it is producing elliptically polarized light it



FIG. 22.—SAME FIELD AS IN FIG. 20.  $\times 350$ .

By slightly rotating analyzing nicol from the crossed position, FeS portion of the inclusion darkens, showing that FeS is anisotropic and has effect of rotating plane of polarization.

cannot be made to darken more than it is at present by rotation of the analyzer, while if it is rotating the plane of polarization, it can. The analyzer was rotated about one degree clockwise and the cause was found. (See Fig. 22.) The ferrous sulfide darkened considerably, becoming as dark as the ferrous oxide. The sulfide therefore has the effect of rotating the plane of polarization. (Of course the lightness of the sulfide in Fig. 21 might have been due to transparency of the inclusion but rotation of the stage settled this point.) If the inclusion were both transparent and surface anisotropic, by rotating the stage to the point where the anisotropic effect had vanished, we should observe the transparency.

### *General Effects*

The three types of inclusions illustrated demonstrate the three general effects that can be obtained. An inclusion can produce anisotropic effects and be so transparent that this is not ordinarily noticed unless internal reflections are eliminated. An inclusion can be trans-

parent and have identifying colors. An inclusion can exhibit anisotropic effects and have no noticeable transparency.

Although a large number of metallic compounds in metals were observed, none of these exhibited detectable anisotropy. Among these were carbides and nitrides in chromium, and most of the ordinary inclusions in aluminum. Either the anisotropy of these inclusions is too small to be detected or surface films obscure the anisotropic effects of the substances themselves. The presence of anisotropy would not necessarily be a rigorous demonstration that an inclusion was normally anisotropic. The substance might very well be in a stressed condition, from which anisotropy might originate.

A precise and sensitive instrument should be developed to investigate the phenomena of this subject more closely. Such an instrument should use objectives corrected for infinity; it should be adaptable to oblique illumination (of the type obtained by stopping down the iris and decentering it), so that light should be incident on the sample with approximately only one angle of incidence and only one angle of azimuth; it should be adaptable to monochromatic illumination, so that precise values of phase differences and rotations could be measured. A Soleil-Babinet compensator should be used to obtain plane polarized light from elliptically polarized light. A tube analyzer should be used so that rays will travel in parallel paths. Such a combination of apparatus will allow the full aperture of an objective to be used and at the same time obtain a dark field of view with crossed nicols. It is very possible that differences in reflectivities and phase changes will be magnified at high angles of azimuth, and anisotropy that is too small to be detectable with ordinary instruments may thus be determined. Such an instrument would also permit the detection of anisotropy in very small particles.

#### THEORY OF OPTICAL CROSS AND CONCENTRIC CIRCLES

In the discussion on oxide in copper, mention was made of the appearance of a dark cross and dark concentric circles. The cross has been noticed in almost all of those inclusions; the rings appear less frequently and are less contrasted.

Hoyt and Scheil<sup>(17)</sup> have observed this phenomenon; Fig. 3 of their paper is an excellent example of a well developed pattern in a glassy silicate. They found that the cross remains stationary with respect to the cross hairs in the microscope when the stage is rotated. In other words, the orientation of the inclusion does not affect the production of the pattern. At any rate, it would not seem possible for a glassy silicate to possess directional properties; any explanation of the phenomenon must therefore not depend on anisotropic effects. Hoyt and Scheil also find that when these round inclusions are elongated by rolling the pattern is no longer developed.

These facts are therefore known: (1) The phenomenon does not depend upon the orientation of the inclusions; (2) isotropic substances such as cuprous oxide can also develop the pattern; (3) the shape of the inclusion is a determining factor. Globular inclusions produce the effect; other shapes do not. Development of the theory has demonstrated that the cross and the concentric circles are produced by independent mechanisms.

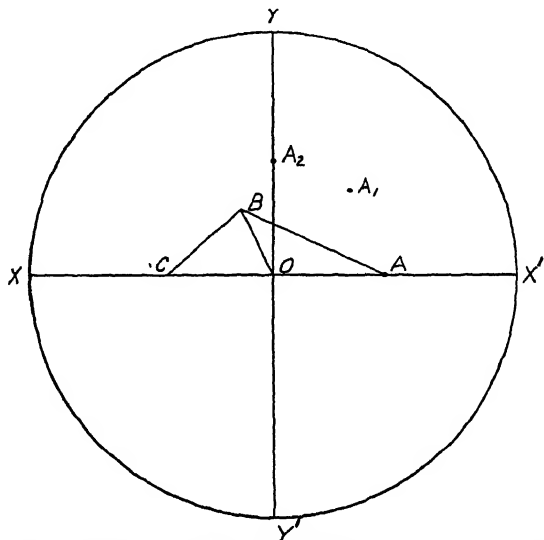


FIG. 23.—SURFACE OF HEMISPHERICAL, TRANSPARENT INCLUSION IN SURFACE OF METAL.

The formation of the cross is directly dependent upon the focusing effect of a spherical surface for its production. For simplicity, a hemispherical shape of inclusion was selected. This inclusion is embedded in the surface of the metal, on which the microscope is focused. Fig. 23 represents a view of the inclusion as it is seen from above.  $O$  is the center of the figure;  $A$  represents a point chosen at random on the surface and is a point under observation on the surface. It is desired to find where on the surface the light that illuminates  $A$  can enter.  $BA$  is any ray of light reaching  $A$  and thus participating in the illumination of that point.  $B$  is the point at which the light is reflected from the metal-inclusion surface.  $OB$  is a normal from  $O$  to the point of reflection. The plane of reflection is therefore  $OAB$ . As the plane of incidence is always the same as the plane of reflection, the incident ray also lies in the plane  $OAB$ . Therefore, whether the light has suffered one, two, or more reflections from the bottom surface of the inclusion, the planes of incidence and reflection are always the same as  $OAB$ . When the light is traced backwards to the point at which it entered the surface, that point is on the trace of plane  $OAB$  on the surface of the inclusion, the line  $XOX'$ . The

only light that can ever reach  $A$  must enter along the diameter on which  $A$  is located. If the particular ray  $B$  had had only one reflection, it might have entered along the path  $CB$ .

In accordance with the theory of the formation of elliptically polarized light described earlier in the paper, the azimuth angle is the angle between the plane of incidence and the plane of polarization. If the azimuth angle is  $0^\circ$  or  $90^\circ$ , no elliptically polarized light can be formed regardless of the phase difference introduced between the parallel and perpendicular components by a reflection, because in these cases there is only one component. When the azimuth angle is  $45^\circ$ , the maximum amount of ellipticity is introduced by any phase difference.

If the plane of polarization is  $XOX'$ , the light emitted from  $A$  or  $A_2$  will still be plane polarized and will be absorbed by the analyzer.  $A$  and  $A_2$  will be relatively dark.  $A_1$ , with an azimuth angle of  $45^\circ$ , will be relatively bright.

Selecting points all over the surface, we find that those on  $XOX'$  and  $YOY'$  are dark; those between are in varying shades of lightness. The lightest are those at  $45^\circ$  to these directions. The resulting figure is the cross, which is observed.

Any roughness of the reflecting surface results in the partial or total destruction of the effect because of the random reflections introduced by this roughness. In the case of a void or gas pocket, the roughness would be greatest because the crystallization of the metal would be least interfered with. This would explain why the optical cross was not observed in voids. An inclusion that solidified above the melting point of the metal would result in the smoothest reflecting surface and the greatest clearness of the cross. Cuprite, which solidifies about  $200^\circ$  above the melting point of copper, gives very distinct optical crosses. An inclusion that solidified below the melting point of the metal would hinder the free crystallization of the metal less and might have a roughened reflecting surface after reflection, resulting in a milky appearance of the inclusion under crossed nicols. This might be the cause of the effect attributed by Hoyt and Scheil to calcium oxide or fluoride.

The concentric dark circles observed in inclusions are due to intensity variations that have no connection with any polarization phenomenon. The polarization microscope enables them to be observed by removing the surface reflections that ordinarily obscure them.

The contrast of the rings depends upon the size of the cone of rays inside the inclusion transmitted by the objective in illumination and observation. The size of this cone depends in turn upon the numerical aperture of the objective and the index of refraction of the transparent inclusion. With a cone of rays restricted to those ordinarily found, there are definite areas on the surface of the inclusion which single, double and other reflections may illuminate. These areas are a circle for single

reflections and rings for other reflections. These areas of brightness may be separated or may overlap, depending upon the size of the cone of rays. In either case, this leaves fewer illuminated areas comparatively dark.

An understanding of this phenomenon may be obtained from Fig. 24, which is a section perpendicular to the surface of a specimen and through the center of a hemispherical transparent inclusion. Each ray of light illuminating the point  $O$  enters at  $O$  and is reflected only once inside the inclusion. Therefore at the center of such an inclusion a cone of rays of  $0^\circ$ , such as  $OB$ , will still illuminate  $O$ . At the point  $A$  the smallest

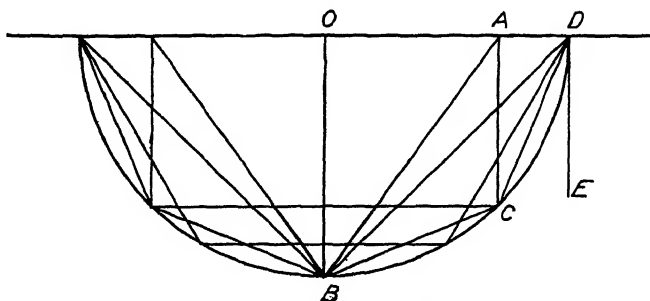


FIG. 24.—CROSS SECTION THROUGH DIAMETER OF HEMISPHERICAL, TRANSPARENT INCLUSION IN SURFACE OF METAL.

cone of rays that will illuminate  $A$  by a single reflection is measured by the angle  $BAC$ . At  $A$ , a cone of rays of  $0^\circ$ , such as  $AC$ , will produce a double reflection, which could illuminate  $A$ . At the extreme point  $D$  the angle of the smallest cone of rays that will illuminate it by a single reflection is the angle  $BDE$ , which is  $45^\circ$ . At any smaller angle there are two, three or more reflections.

If we plot the distances from the center at which single, double, etc., reflections can occur against the smallest size of the cone of rays that will permit such reflection to occur, the graph will show the size of the cone of rays required for a certain type of reflection at a certain point. Fig. 25 is such a graph.  $AM$  is the line of single reflections. Single reflection will occur in the area  $ABCM$ . Below the line  $AM$  no single reflections can occur.

Graphical computations for two, three and four reflections gave the other results plotted in Fig. 25.  $BEJC$  is the area within which double reflection will occur,  $KFIC$  the area within which triple reflection will occur, and  $LGHC$  the area in which quadruple reflection will occur. A minimum intensity will occur at  $N$ , where the smallest part of any cone of rays is producing reflections that illuminate points the given distance from the center. The distance is 0.57 times the radius. The next minimum is at  $O$ , a distance of 0.84 times the radius from the center. A much less marked minimum is at  $P$ . There are other minima for higher order reflections, but they are even less marked.

Fig. 3 of Hoyt and Scheil's paper was closely examined. The position of the rings was not symmetrical with respect to the center of the inclusion, indicating that the inclusion is not perfectly spherical. This is also apparent from their photomicrograph of the same inclusion by

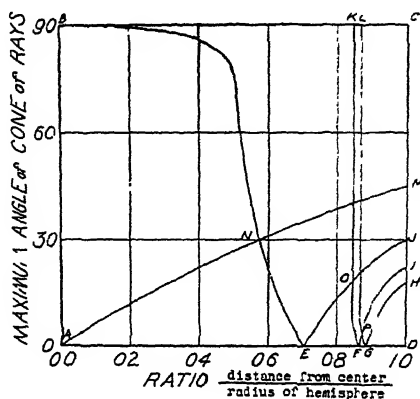


FIG. 25.—GRAPH SHOWING REGIONS IN WHICH SINGLE, DOUBLE, TRIPLE AND QUADRUPLE REFLECTIONS CAN TAKE PLACE.

ordinary light. Only the first two rings are distinct, as would be expected from the above theory. The ratio of the diameter of the inner ring to that of the outer was measured as closely as it could be. The ratio was 0.59. The above theory predicts that 0.68 should be obtained. In view of the distortion of the inclusion, this is considered by the writer to be evidence of the correctness of the theory.

### CONCLUSIONS

From a study of the metallurgical polarization microscope the following conclusions were reached:

1. Anisotropy can be detected in many instances where it should occur, the effects are very much smaller than in studies of transparent substances. Sometimes anisotropy should be present but is not apparent; owing either to the smallness of the anisotropy or to the presence of surface films.
2. Surface films were observed on the metal zinc.
3. Anisotropy due to strain could not be detected. As all anisotropic effects of reflection are small, it is probable that the effects are too small to be detected.
4. The instrument can be very useful in the identification of inclusions. It can detect either surface anisotropy or transparency of the inclusion if they are present in sufficient amounts. If both are present in detectable amounts, the intensity of one will usually predominate. Ways of distinguishing between anisotropy and transparency are given. Three general types of inclusions are illustrated.



5. The present instrument is imperfect; ways of improving it are discussed.

#### ACKNOWLEDGMENT

The writer thanks Dr. M. A. Hunter, of Rensselaer Polytechnic Institute, for advice and suggestions throughout the course of the investigation. He is very grateful to Dr. G. H. Carragan, of Rensselaer, and Dr. H. W. Russell, of Battelle Memorial Institute, for their assistance with the manuscript.

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#### DISCUSSION

(Eric R. Jette presiding)

S. L. HOYT,\* AND M. A. SCHEIL,\* Milwaukee, Wis. (written discussion).—The author is to be congratulated upon his paper; in no other place in the literature is there as concise and simple a treatment of the theory of reflected polarized light

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\* A. O. Smith Corporation.

phenomena. In our own use of reflected polarized light we have attempted to apply one particular feature of the metallurgical polarizing microscope; namely, to study anisotropic effects produced by permanently straining iron or steel. Like the author, we found that low-powered objectives were better suited to this examination, but the anisotropy produced was so elusive a thing that we did not go far into the work in this direction.

In considering the author's work on typical inclusions in chromium metal, it is doubtful whether  $\text{TiO}_2$  or  $\text{CrO}$  inclusions ever occur free from considerable amounts of  $\text{FeO}$  and  $\text{SiO}_2$ , at least in ferrous materials. Our examination of various lots of ferrochromium (70 per cent Cr) has shown duplex inclusions, such as the author shows in Figs. 16 and 17. We find in our samples that the eutectic described by the author exhibits anisotropic character and the light gray angular or cubical oxide inclusions are usually opaque, but are sometimes transparent when the residual silicon suggested that they were contaminated with  $\text{SiO}_2$ . The birefringent optically anisotropic crystalline inclusions described in our paper,<sup>17</sup> and shown there as Figs. 20 and 21, were analyzed and found to contain about 60 per cent  $\text{Al}_2\text{O}_3$ , 30 per cent

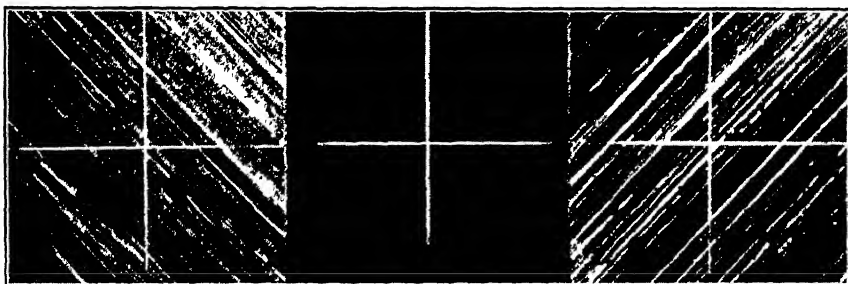


FIG. 26.

FIG. 27.

FIG. 28.

FIGS. 26-28.—SCRATCHES ON STAINLESS STEEL ROTATED THROUGH  $90^\circ$  BETWEEN CROSSED NICOLS.  $\times 500$ , REDUCED  $\frac{1}{2}$  IN REPRODUCTION. VIBRATION DIRECTIONS OF NICOLS INDICATED BY WHITE CROSSES.

$\text{Cr}_2\text{O}_3$ , 7 per cent  $\text{SiO}_2$ , 2 per cent  $\text{FeO}$  and 1 per cent  $\text{MnO}$ . It may be possible that the anisotropic effects of the author's inclusions are due to  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$  contaminations as he melted the chromium metal in an alundum crucible in vacuo.

The theory of the optical cross and concentric circles as given by the author appears as a reasonable explanation of these phenomena. Regarding the metal-inclusion interface having a roughened reflecting surface, the particular inclusions we described showing the optical cross and concentric rings appeared to us to be particularly smooth. This fact has been observed several times for both clear glass and milky inclusions, so that we attribute opalescence to some contamination of the glassy inclusions and not to a roughening of the metal-inclusion interface. Although this may be possible, we have not observed it.

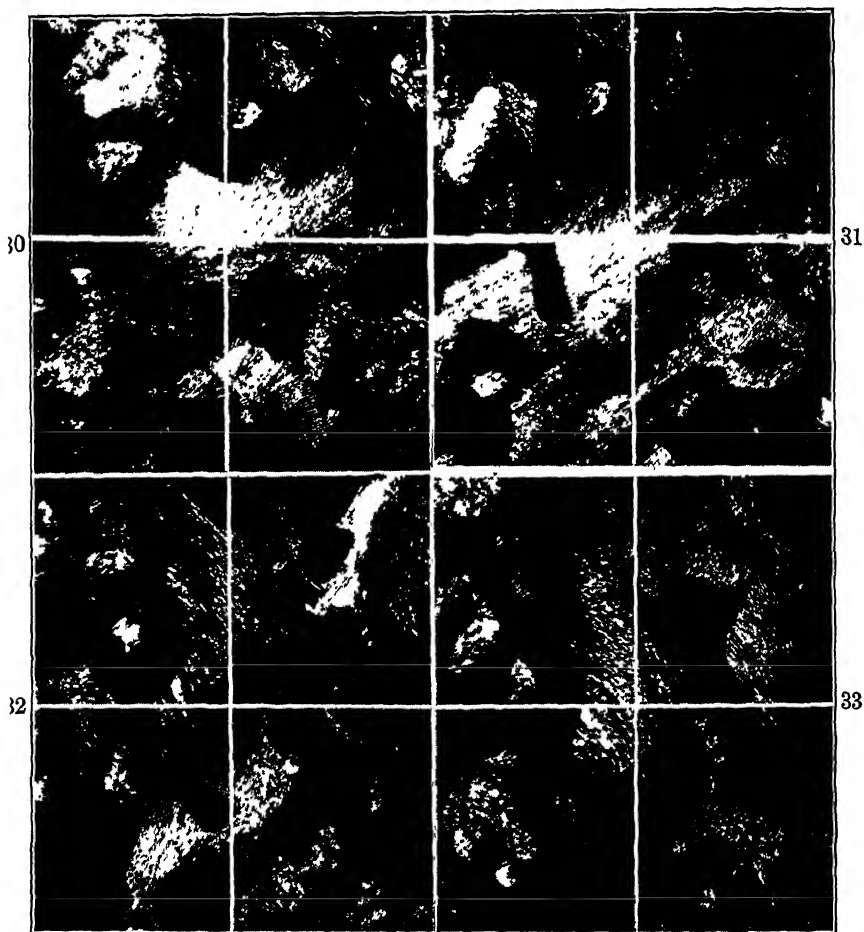
M. BAEYERTZ,\* Chicago, Ill. (written discussion).—Mr. Dayton has mentioned the effect of certain types of roughness of a reflecting surface in producing behavior that might superficially be mistaken for true anisotropism. In this connection the accompanying photomicrographs may be of interest to metallurgists. Figs. 26 to 28 show fine parallel scratches on a piece of 18 per cent chromium, 8 per cent nickel stainless steel, which contained less than 0.10 per cent carbon. The scratched surface was photographed by incident plane polarized light and was rotated between crossed

\* Illinois Steel Co.



FIG. 29.—PEARLITE AREA *a* WITH CURVED LAMELLAE.  $\times 500$ .

FIGS. 30-33.—PEARLITIC AREA *a* ROTATED BETWEEN CROSSED NICOLS,  $\times 500$ . VIBRATION DIRECTIONS OF NICOLS INDICATED BY WHITE CROSSES.



nicals. Fig. 29 shows an area of pearlite, *a*, with curved lamellae photographed by ordinary incident light. Figs. 30 to 33 show the same area when rotated between crossed nicols. The white cross drawn on the area *a* in each figure indicates the vibration directions of the nicols. The pearlite area *a* appears dark when the fine parallel cementite lamellae are parallel or at right angles to the vibration direction of the incident plane polarized light. In all other positions light passes the analyzer, reaching a maximum intensity of  $45^\circ$  to the vibration direction of the incident light. The case of the parallel scratches and the parallel cementite lamellae are analogous. The effect is due entirely to the production of fine parallel grooves on the surface by etching away the ferrite and leaving the cementite lamellae in relief. A similar explanation applies to etched martensite. The observations that occasioned these photomicrographs were made about a year ago. To date, except in certain non-metallic inclusions, we have not observed true anisotropism in any of the constituents of steel.

C. S. SMITH, Waterbury, Conn. (written discussion).—The customary method of examination of sections under the microscope, as described so well in this paper, requires the use of both polarizing and analyzing prisms, and depends on the optical properties of the surface being studied. It does not seem to have been recognized hitherto that certain lamellar structures themselves polarize light and that this polarization, combined with the analyzing effect of the plane glass type of illuminator, is of considerable importance in the resolution of the structures. While the simple theory of the grating does not require polarization of the diffracted light, it is apparent that such polarization does occur to a varying extent in ruled gratings, and my experiments have shown that a typical pearlitic structure when etched produces a considerable degree of polarization. This is important in the resolution of such structures, since the polarizing effect of the illuminator results in the differentiation of neighboring eutectoid colonies and is responsible for giving sufficient contrast between the lamellar phases to permit them to be seen without a heavy staining etch.

Fig. 34 shows a number of eutectoid colonies forming near the boundary of a large grain of the beta phase in the copper-aluminum system. This photograph, taken using a prism illuminator, should be compared with Fig. 35, of the same field, using the plane glass illuminator. That the differentiation between grains in the latter is due to polarization was shown by rotating the specimen through  $90^\circ$ , leaving the illumination unchanged, when the grains previously light became dark, and vice versa\* (Fig. 36). The plane glass illuminator does not completely polarize, and better contrast between colonies is obtained if the prism illuminator is used in conjunction with a single nicol, placed either before the illuminator or behind the objective or eyepiece. Any grain, depending on the orientation of the section of the plates on the surface, may be made either light or dark according to its relation to the plane of polarization of the incident light. This is shown by Figs. 37 and 38.

At high magnification, where the plane glass illuminator is normally used and where the lamellae can be separately resolved, polarization is important in giving sufficient contrast between the two phases to permit their recognition. The marked difference in appearance between Figs. 39 and 40 illustrates this. The difference is due solely to rotation through  $100^\circ$  of a nicol prism placed behind the eyepiece. Note that it is the surface direction of the lamellae, which varies from place to place, and not the actual orientation of its lattice (which presumably remains the same through-

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\* It has been suggested that the effects are due to obliquity of illumination. It should, therefore, be mentioned that in all cases the illumination was "critical" and, when using the glass illuminator, perfectly vertical. The prism necessarily introduces some obliquity, but evidently not enough to cause grain differentiation on that account (Fig. 34).



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FIG. 34.—EUTECTOID AREAS IN PARTLY DECOMPOSED ALUMINUM-COPPER ALLOY. PRISM ILLUMINATOR.  $\times 75$ .

FIG. 35.—SAME FIELD AS FIG. 34. PLANE GLASS ILLUMINATOR. NO NICOL.

FIG. 36.—SAME AS FIG. 35. ILLUMINATION UNALTERED. SPECIMEN ROTATED  $90^\circ$ .

FIG. 37.—SAME FIELD. PRISM ILLUMINATOR. NICOL POLARIZER. NO ANALYZER.

FIG. 38.—SAME FIELD. PRISM ILLUMINATOR. NICOL ROTATED  $90^\circ$  FROM POSITION IN FIG. 37. NO ANALYZER.



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out a given grain of the eutectoid) that determines whether a lamella should be dark or light.

It should be emphasized that the effect is quite different from the *rotation* of the plane of polarization on which the use of the polarizing microscope depends. It is an actual *polarization* of the light, and needs but a single nicol to detect it, whereas the rotational effect requires both polarizer and analyzer.

A rather curious effect of the polarization of light by eutectoids is the one that led the writer to detect it. Using a monobjective binocular microscope, the semi-reflecting prism acts as a partial analyzer and sends light polarized in directions  $90^\circ$  apart to the two eyes. As a result a eutectoid grain appearing bright to one eye is dark to the other, while the non-polarizing groundmass remains of uniform brightness.

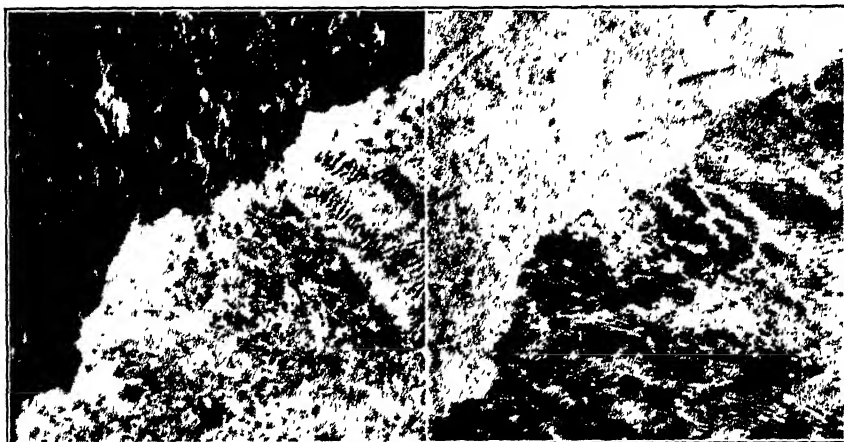


FIG. 39.

FIG. 40.

FIG. 39.—SAME SPECIMEN,  $\times 750$ . PLANE GLASS ILLUMINATOR. EYEPiece ANALYZER. NO POLARIZING NICOL.

FIG. 40.—SAME FIELD. ANALYZING PRISM ROTATED  $100^\circ$  FROM POSITION IN FIG. 39.

R. W. DAYTON (written discussion).—These additions to the subject are most welcome. The phenomenon discussed by Mr. Smith is, as far as I know, new to the literature. The same basic reasoning will apply to the polarization of light by a lamellar structure as to the anisotropy a lamellar structure exhibits in polarized light. The only difference is that in the former we are concerned with the greater reflectivity of one of the two components of polarized light; in the latter, with the phase difference produced between these components.

As Mr. Smith suggests, this phenomenon may be an aid in developing contrast in metallography by ordinary light.

## Solubility of Oxygen in Solid Cobalt and the Upper Transformation Point of the Metal\*

BY A. U. SEYBOLT,† JUNIOR MEMBER A.I.M.E., AND C. H. MATHEWSON,‡  
MEMBER A.I.M.E.

(Chicago Meeting, October, 1935)

As is well known, many questions affecting the properties and uses of a metal cannot be answered without careful consideration of the state of purity realized in the various operations of preparation, refining, or special treatment that have brought the product to its final state. The occurrence of an impurity in minute quantity offers no guarantee that its effect will be inconsiderable because dissolved substances often modify the properties of a metal quite out of proportion to their concentration. In such cases the determination of solid solubility must be accepted as a problem of considerable difficulty, requiring the use of especially purified materials and methods not ordinarily used in the metallurgical laboratory.

This aspect of the equilibrium between metals and their oxides is especially important and a search for fundamental data reveals little except conflicting opinion even concerning the systems of common occurrence and interest. Rhines and Mathewson<sup>1</sup> in 1934 studied the solubility of oxygen in solid copper by annealing to equilibrium in air and gave reasons for the failure of other methods, notably the ordinary procedure of heat-treatment followed by microscopic examination, to yield reliable results.

In this paper, a similar study has been made of the solubility of oxygen in cobalt. The simple theory of this method is outlined below.

### CONDITIONS OF EQUILIBRIUM BETWEEN A METAL AND DISSOLVED OXIDE AT DIFFERENT TEMPERATURES AND PRESSURES

The general conditions of equilibrium in any system are conveniently summarized in a projection of the triple curves of the  $P$ ,  $T$ ,  $X$  space

\* From a part of a dissertation to be presented by A. U. Seybolt to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Manuscript received at the office of the Institute June 10, 1935.

† Graduate Student, Department of Metallurgy, Yale University, New Haven, Conn.

‡ Professor of Metallurgy, Yale University.

<sup>1</sup> References are at the end of the paper.

figure in the pressure-temperature plane. When oxygen is combined with cobalt and brought into equilibrium with the prevailing excess of metal, the system under consideration is Co-CoO. In order to develop a true representation of the type of equilibrium that exists in this system, we need to start with full information concerning the stability of the oxide; i.e., whether it melts entirely without decomposition, or dissociates either on melting or in the solid state, in addition to a knowledge of the underlying polymorphic transformations of cobalt. Then, the details of binary association between these components, such as the eventual occurrence of a eutectic mixture, or biliquidal phenomena, are needed to complete the picture.

None of these facts are available in precise form but the accompanying diagram (Fig. 1), revealing the nature of the required approximations, makes it apparent that these deficiencies do not affect the wide expansive field of coexistent cobalt solution and oxide (solution) to the left of point  $Q_1$  in which the present method is operative, except that this field is divided by transformation boundaries into sub-regions containing alpha, beta, and gamma cobalt; the present experiments themselves offering evidence concerning the location of the beta and gamma regions.

According to von Wartenberg and Gurr<sup>2</sup>, the melting point of CoO, previously unknown, is 1935° C., far above the melting point of cobalt (approx. 1480° C.) and melting in air at atmospheric pressure is not accompanied by any great amount of volatilization. This points to low vapor pressures for CoO but in Fig. 1a the triple point CoO is placed above the triple point Co, on the assumption that the vaporization curve of the compound lies between the curves of its components, cobalt and oxygen. The development of a type diagram corresponding to higher vapor pressures for Co than for CoO would not alter the final conclusion with respect to the present problem.

Microscopic observations in this laboratory indicate that cobalt oxide and cobalt, like nickel oxide and nickel, form a eutectic close to the composition and melting point of the metal component, and the near-eutectic region of the primary curve of oxide separation suggests a biliquidal condition in regions of higher oxide concentration, as is usual in systems of this nature.

These conditions are expressed in Fig. 1a by including the quadruple points  $Q_1$  corresponding to coexistence of gas, cobalt-rich liquid, cobalt oxide and cobalt, and  $Q_2$ , representing gas, liquid rich in cobalt oxide, cobalt-rich liquid and cobalt oxide. The transformations that take place when the triple curves are traversed by changing temperature or pressure are written alongside the curves in the sense of a movement from right to left through the fields of the diagram; i.e., the effect of falling temperature.





For the immediate purpose it may be noted that at temperatures below  $Q_1$  and pressures above the gas-condensation curve designated,  $G = \gamma \text{ Co soln.} + \text{CoO}$ , that lies at insignificantly low pressures, the system is entirely condensed to solid according to the designation, "Field of  $\gamma \text{ Co soln.} + \text{CoO}$ ."

The orthodox method of reaching this field would be by movement from right to left through the diagram; i.e., by cooling the molten alloy through the eutectic temperature at the atmospheric pressure level.

But it is difficult to determine the amount of oxygen dissolved in the cobalt, the problem set for this investigation, when the alloy also contains cobalt oxide as an (eutectically) associated constituent, and the result can be achieved in another way. If the oxygen of the air is allowed to react with cobalt in this region of pressure and temperature, it should reach the designated condition of equilibrium, saturating the metal at the temperature chosen and building up an excess of CoO on the surface. It is true the pressure concept applying to this field does not call for an oxygen atmosphere, but signifies that any mechanical pressure effect within its boundaries will maintain the stability of the two phases in question. If oxygen itself or the ordinary atmospheric mixture of nitrogen and oxygen, presenting oxygen in great excess, supplies this pressure, the result will be chemical oxidation at the outer surface beyond the composition CoO, but reduction at the inner surface will maintain the association of the two desired phases, cobalt solution and CoO (solution) in the required pressure environment.

Furthermore, the absence of gas as a factor of equilibrium in this part of the diagram justifies the belief that the solid solubilities of Co and CoO in one another will not vary sensibly with the pressure. A pressure-concentration diagram for temperature,  $t$ , is shown in Fig. 1b. The points  $A$  and  $B$  are taken from the sublimation curves of metal and oxide, respectively, as shown by the dotted lines, and the point  $c$  comes from the triple curve receding from  $Q_1$ . The three concentrations assumed to correspond with this  $PT$  point on the triple curve are ( $a$ ) for the metal-rich solid solution, ( $b$ ) for the gas, and ( $c$ ) for the oxide-rich solid solution. Above the reaction horizontal  $acb$  the two saturated solid solutions are in equilibrium and the boundaries of the field are drawn vertically to indicate the insignificant effect of pressure on the solubilities. Below  $acb$ , where gas is in equilibrium with the metal-rich solution on the left and the oxide-rich solution on the right, the solubility varies greatly with the pressure.

In determining solid solubility by interdiffusion of the two solid phases any pressure of the gas conveying oxygen to the metal above the insignificantly low value at  $acb$  would appear to be satisfactory and no care need be taken to maintain it constant. Practically, the metal is

allowed to saturate itself with atmospheric oxygen at the desired temperature, cleaned from oxide scale, and analyzed.

It was arbitrarily assumed in drawing Fig. 1*a* that CoO is completely stable at all temperatures. However, the conditions of lesser stability represented by Fig. 1*c* on melting and Fig. 1*d*, dissociation prior to melting, may be substituted in Fig. 1*a* in the region around  $Q_2$  without changing the conditions below  $Q_1$ , which alone are important in the present connection. In Fig. 1*c*,  $S$  is the highest realizable point on the sublimation curve of the oxide and  $M$  the lowest realizable point on the melting curve. In Fig. 1*d*,  $S$  is reached before melting occurs.

In the present investigation one solubility curve was obtained in the region through which the dotted line  $t$  is drawn and another in the region traversed by  $t_1$ , thus pointing to a transformation temperature ( $875^\circ\text{C.}$ ), within the range of experimentation. But the literature contains ample evidence of a transformation at a much lower temperature (around  $450^\circ\text{C.}$ ) quite outside the range of present experimentation. To account for these two transformations, the diagram, Fig. 1*a*, gives recognition to three forms of cobalt, designated according to usual practice alpha, beta and gamma in the order of ascending temperature.

There is, of course, some doubt as to the vapor-pressure relations between these different crystalline phases of cobalt, but it is here assumed that they are reversible, even though indifferently so, in the ordinary enantiotropic sense. Some discussion of this subject is introduced later on.

#### MATERIALS AND EXPERIMENTAL PROCEDURE

Cobalt in the form of cathode plates approximately  $1\frac{1}{2}$  in. square and  $\frac{1}{8}$  in. thick was procured from the Central Trading Co. of New York. This material was represented to be at least 99.5 per cent pure. Spectrographic analysis indicated it to be of a somewhat higher purity. Traces of iron, nickel, copper and lead were found, but all the persistent lines were very faint.

The principle of the method used to obtain an equilibrium oxygen content in cobalt has just been described. The actual procedure was to soak the metal in an oxygen atmosphere at the temperature chosen, for a sufficient time to obtain equilibrium by diffusion of oxygen through it.

To ascertain first if there was any appreciable solubility, a cobalt cathode plate was sawed in two and both pieces placed in a tube furnace with the ends open to insure a moving stream of air. The specimens were heated to  $800^\circ\text{C.}$  and the temperature was held constant to about  $\pm 5^\circ\text{C.}$  for three days by means of a Leeds & Northrup controlling potentiometer. At the end of this time, one of the pieces was quickly quenched in cold water, while the other was held at  $400^\circ\text{C.}$  for an additional 36 hours.

Both pieces were polished for microscopic examination, and are shown in Figs. 2 and 3. The specimens were unetched. The piece that was quenched from 800° C. shows nothing but a blank surface except for an occasional spot of cobalt oxide that was not retained in solution, owing to an insufficiently rapid quench. The other shows a considerable amount of cobalt oxide that was precipitated from solution by the aging treatment at the much lower temperature. This then indicates that there is a distinct solubility of oxygen in solid cobalt; and, further, that the solubility increases with temperature.

A schedule of soaking operations was next planned to cover the temperature range from 600° to 1200° C. Temperatures lower than

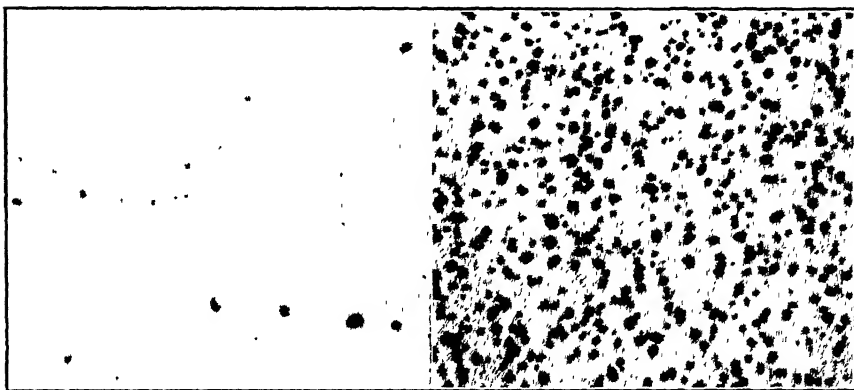


FIG. 2.

FIG. 3.

FIG. 2.—COBALT SOAKED IN AIR AT 800° C. FOR THREE DAYS, THEN QUENCHED IN WATER.  $\times 100$ .

FIG. 3.—COBALT SOAKED IN AIR AT 800° C. FOR THREE DAYS, THEN ANNEALED AT 400° C. FOR 36 HOURS.  $\times 100$ .

600° C. were avoided, as reactions in the solid state are apt to be quite slow even at this temperature. It developed, however, that equilibrium was attained much more rapidly than was anticipated in the selected range of temperature.

#### EFFECT OF NITROGEN

As it was planned to conduct the soaking operations in an atmosphere of air rather than in pure oxygen, it was considered advisable to test the effect of the nitrogen of the air on the equilibrium oxygen content at some definite temperature. This was done by soaking for three days at 810° C.; one specimen in air, the other in tank oxygen. At the end of this time both specimens were analyzed and the oxygen contents were found to be identical. This result was anticipated on the basis of a recent communication by Sieverts<sup>3</sup>, who attempted to measure the solubility of nitrogen in solid cobalt, but failed to find any. Accordingly the rest

of the treatments were carried out as planned in air, except with the 600° C. specimens, which had been previously prepared in oxygen.

### TIME FOR SATURATION

The end point for saturation at any temperature was determined by the obvious expedient of repeated soaking and analysis until the oxygen content had reached a constant value.

The highest temperature contemplated, 1200° C., was selected for the first test because equilibrium would be expected to occur in a relatively short space of time. Thus the time required to get a given specimen ready for analysis was small, and repeat soakings could likewise be accomplished quickly. As Table 1 shows, less than three hours were sufficient at this temperature. At the lowest temperature, 600° C., the time of soaking was increased to a period of one week, thus offering the practical certainty that equilibrium would be reached. At intermediate temperatures, prorated annealing treatments (proportional to about the 6th power of the temperature) were conducted. In no case did the first soaking period fail to be sufficient. The results given in Table 1 were considered satisfactory, and no work was attempted to find the minimum time of soaking for saturation.

TABLE 1.—*Temperature-time Values for Saturation of Cobalt with Oxygen*

Temperature, Deg. C.	Period of Soaking, in Air Except Where Otherwise Indicated	Oxygen Content, Per Cent
600	7 days (in oxygen)	0.006
600	12 days (in oxygen)	0.006
700	7 days	0.009
810	3 days (in oxygen)	0.016
810	7 days (in oxygen)	0.015
810	7 days	0.016
875	3 days	0.010
945	2 days	0.007
945	4 days	0.007
1000	21 hr.	0.008
1000	29 hr.	0.008
1200	3 hr.	0.013
1200	6 hr.	0.013

Evidently, however, the time for penetration of the cobalt specimens by the oxygen atoms is short compared to that required for many proc-

esses of diffusion. A rather simple but possibly incomplete explanation of this rapid diffusion is as follows:

When the metal is placed in an oxidizing atmosphere at some elevated temperature, there is a difference of about 20 per cent between the surface content of oxygen and the oxygen in the interior of the metal. The latter value, of course, is zero, and the 20 per cent value is merely the oxygen content of the oxide,  $\text{CoO}$ .

Since the final oxygen content of the metal is very small, this initial driving force of some 20 per cent of oxygen persists all through the soaking process, thus permitting saturation in a short time. On the other hand, in order to deoxidize the metal by means of hydrogen, as in the Ledebur method for oxygen analysis, a much longer time is required. Two hours at  $1100^{\circ}\text{C}$ . in a hydrogen atmosphere was found necessary to deoxidize metal chips about 0.005 in. thick. But the same metal about 0.2 in. thick becomes completely saturated at  $1200^{\circ}\text{C}$ . in an oxygen atmosphere after approximately the same period. Here, the driving force of deoxidation is only the difference between zero per cent of oxygen at the surface of the chips where the hydrogen is constantly reacting to reduce the oxide present and a few hundredths of a per cent of oxygen in the interior of the metal.

In Table 1 the temperatures for which only one soaking period is shown are those for which the period had already been found sufficient at a lower temperature.

#### METHOD OF ANALYSIS

The oxygen-containing samples were analyzed by the Ledebur method of weighing the water formed by reduction of the metal chips by hydrogen in a fused silica tube at  $1100^{\circ}\text{C}$ . Great care was taken to remove all traces of surface oxidation before cutting chips for analysis. The most efficient method found for this purpose was to immerse the oxide-covered metal in molten borax glass contained in a nickel crucible. The borax effectively fluxed the cobalt oxide to a glassy slag that could be dissolved easily in hot hydrochloric acid. After this treatment the metal surface was clean and bright without a trace of surface oxide. The next step was to cut chips from the cobalt plates in a clean shaping machine, every precaution being taken to exclude all oil and grease. The cobalt chips varied in thickness from less than one thousandth to about seven thousandths of an inch.

To remove surface oxidation from the chips, they were heated in purified hydrogen at  $500^{\circ}\text{C}$ . prior to the high-temperature reduction that removed the oxide contained in solid solution. This expedient for removing surface oxide was suggested by Larsen and Brower<sup>4</sup> in their work on a modified Ledebur method for the determination of oxygen in

steel. While these workers commented that 2 hr. was required to remove the surface oxide from steel, one hour was found to be enough in the case of cobalt. That this treatment sufficed to remove all surface oxide was easily proved by placing a piece of heavily oxidized cobalt in the reduction tube and giving it the low-temperature reduction mentioned above. Afterwards, the tube was cooled to room temperature, and the surface of the metal was found to be clean and bright. To prove that no internal oxide was removed by the one-hour reduction at 500° C. is more difficult. Perhaps it will suffice to remark that, since 2 hr. at 1100° C. was found necessary to completely reduce the oxide, the amount of oxygen that could diffuse out at the comparatively low temperature of 500° C. must be minute indeed. It is noteworthy that the amount of surface oxidation did not appear to be connected with the amount of oxygen in the metal, as good checks were obtained in the main experiments following this preliminary treatment.

The apparatus actually used was designed after the one employed by Rooney<sup>5</sup>, who analyzed the iron-oxygen alloys of Tritton and Hanson described in their well-known paper on the iron-oxygen system. Certain improvements, however, were made, especially in the water absorbent. While Rooney used calcium chloride in his weighing tube, it was found in this work that anhydrous could be depended upon to effectively remove all traces of water vapor from the damp hydrogen. This substance was the most satisfactory of several dessicants tried.

Other than indicated above, the oxygen analysis is essentially the same as the one described by Rooney. As is evident from the data given in Table 1, after the train had been in use for a time and the fused silica tube "broken in" by a previous 8-hr. heating at 1100° C. with hydrogen passing through it, no difficulty was experienced in obtaining good checks. The fused silica tubes, however, became porous after about 20 runs and had to be discarded.

## RESULTS AND DISCUSSION

Perhaps the most interesting single fact about the curve of solid solubility of oxygen in cobalt is the striking discontinuity at 875° C. There can be no doubt that this represents the transformation of cobalt from the face-centered cubic lattice existing below this temperature to the close-packed hexagonal form stable in the higher region. The lower solubility of oxygen in the latter form of cobalt requires a transformation horizontal above the transition temperature in the pure metal, as shown, but this temperature difference must be small on account of the small solubilities involved.

The first crystallographic evidence of a high-temperature transformation in pure cobalt was found by Hendricks, Jefferson and Schultz<sup>6</sup> in

1930. They reduced  $\text{Co}_3\text{O}_4$  in hydrogen at various temperatures from  $310^\circ$  to  $1100^\circ$  C. and found by X-ray analysis that metal prepared below  $400^\circ \pm 20^\circ$  C. was entirely of the hexagonal close-packed form. Above this temperature the resulting cobalt powder was face-centered cubic, until the hexagonal phase appeared again at  $1015^\circ \pm 20^\circ$  C., along with some cubic cobalt. The low-temperature transformation had been well established, but this was the first convincing evidence supporting the existence of a higher temperature transformation.

In 1933 Sykes<sup>7</sup> repeated the work of Hendricks, Jefferson and Schultz and came to the same conclusion regarding the transformation at about  $1020^\circ$  C.

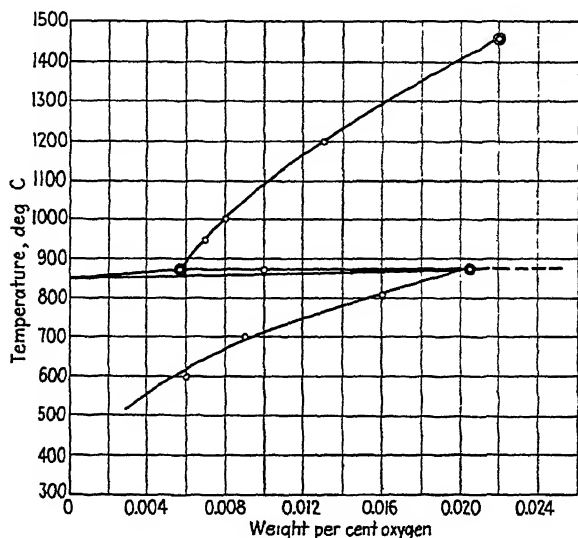


FIG. 4.—SOLUBILITY OF OXYGEN IN SOLID COBALT.

Cardwell<sup>8</sup>, in 1929, worked on the metal cobalt with the intention of locating crystallographic transformations by means of thermionic and photoelectric emission. He found a marked discontinuity in both of these properties at  $850^\circ$  C. in a strip of cobalt of 99.9 per cent purity. Referring to Masumoto's<sup>9</sup> work on the low-temperature transformation in cobalt, Cardwell stated that very likely the discontinuity that he found was the one reported by Masumoto to occur at  $440^\circ$  C. Cardwell's reason for believing this was based on the assumption that the purer the cobalt, the higher would be the transformation temperature. It seems hardly likely, however, that Masumoto's cobalt could have been so impure as to reduce the true transformation temperature some  $400^\circ$  C.

The only other worker known to us as a contributor of data on the high-temperature transformation is Utterback<sup>10</sup>, who measured the total radiation from cobalt over a wide range of temperature and found



discontinuities at 399° and 1047° C. These results agree quite well with those of Hendrick, Jefferson and Schultz<sup>6</sup> and Sykes<sup>7</sup>. Utterback, however, sought to correlate the high-temperature discontinuity with the Curie point.

### ELECTRICAL RESISTIVITY EXPERIMENTS

Having found the evidence described above of a transformation in the cobalt-oxygen alloys, it was considered advisable to try to correlate definitely the reaction horizontal with the transformation in pure cobalt. The measurement of electrical resistivity was chosen for this purpose.

The first specimen used for these tests was made by sawing slots in a plate of electrolytic cobalt, as received, in such manner as to increase its effective length, and bring its total resistance to a value that could be easily measured.

The resistivity was measured indirectly by making the specimen part of an electrical circuit which included a standard one-ohm resistance. The drop in electrical potential across the specimen was read at close temperature intervals by a Leeds & Northrup type K potentiometer, and compared to the potential drop across the standard resistance. Since the value of the standard resistance remained constant at one ohm, the resistance of the specimen could be calculated by simply dividing the voltage across the specimen by the voltage across the standard resistance.

To prevent oxidation of the specimen, it was placed inside a fused silica tube closed at one end, in and out of which was passed a slow stream of purified hydrogen.

### RESISTIVITY RESULTS AND GENERAL DISCUSSION

The resistivity results obtained with the electrolytic specimen proved to be complicated although a definite break at 875° C., the temperature of the reaction horizontal in the constitutional diagram, was found when the specimen was first slowly heated to 1050° C.

In order to eliminate as far as possible any effect on the resistivity curves that might be derivable from its electrolytically deposited condition, another specimen was prepared by hot-rolling at approximately 900° C. to a reduction in thickness of 15 per cent.

Greater reductions than this were found possible, but only at the expense of creating numerous small cracks throughout the metal. Such specimens were avoided in these experiments on account of the uncertain effect of the cracks on the electrical resistance at different temperatures.

Even with the hot-rolled specimen, it was discovered that numerous heatings to the neighborhood of 1100° C. were necessary to get the metal into a reversible condition as regards the temperature of the upper and lower transformations.

Fig. 5 is a resistivity-temperature curve for heating and cooling as indicated by the arrows. The material used was hot-rolled cobalt that had been heated to 1100° C. several times as a preliminary "normalizing" measure.

The low-temperature transformation occurred on both heating and cooling at about 440° C., which is the temperature commonly reported in the literature for this transformation. The fact that it occurred on both heating and cooling and in the correct temperature region is in itself a good indication that the cobalt had reached a stable condition.

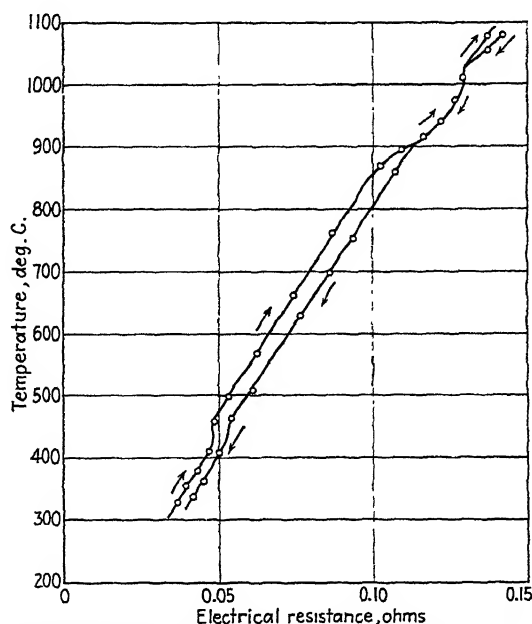


FIG. 5.—TEMPERATURE-RESISTANCE CURVES FOR HOT-ROLLED COBALT.

Of greater interest is the double arrest shown in the upper portion of the curves, corresponding to the transformation found in the oxygen-solubility experiments. The beginning of this arrest occurs well below 900° C. and the end at about 1020° C. It must be concluded that the region from about 875° to 1020° C. is one in which both the face-centered cubic and hexagonal close-packed lattices are present under the conditions of heating and cooling (both 4° to 5° per minute) in these experiments. It is, in fact, a region of considerable indifference, or slow accommodation, to the transformation requirement.

This probably explains why the transformation is not easily picked up by resistivity measurements, or by other physical tests.

Thus, Schultz<sup>11</sup> conducted resistivity work on cobalt and found the Curie point and the lower transformation, but not the upper one.

Sykes<sup>12</sup> reported that he was able to find a thermal arrest in solid cobalt at the lower transformation, but could detect no change in the neighborhood of 1000° C., where he had previously found evidence of the high-temperature transformation by the method of Hendricks, Jefferson and Schultz<sup>6</sup>. Commenting on the sluggishness or incompleteness of the low-temperature transformation in cobalt, Sykes<sup>7</sup> writes, "When once formed, the hexagonal close-packed lattice is very stable. Its pattern persists with but slightly lowered intensity even after heating for 200 hr. at 800° to 1000° C."

This evidence is cited to show that both transformations are indeed slow, and are apt to be incomplete in ordinary heat-treating procedures. Heating and cooling at the rate of 5° C. a minute, the rate approximated during the resistance observations on which Fig. 5 is based, was certainly not slow enough to allow the transformation to occur at a constant temperature.

It is conceivable that cobalt produced by reduction of the oxide by hydrogen in the experiments of Hendricks, Jefferson and Schultz, and of Sykes may need considerable time to assume its stable lattice when formed in the indifferent region just above the upper transformation point, and that their value for the transformation temperature, around 1020° C., is merely the upper limit of this indifferent region, as might be predicted from our curve of electrical resistance (Fig. 5). Perhaps the oxide powder when suddenly treated with hydrogen at a temperature well above the true transformation point absorbs heat so rapidly that it automatically cools into the region of cubic cobalt, much as substances are cooled by evaporation. Or, if suddenly brought into the desired temperature environment, it may reduce to cubic cobalt during the brief heating period and fail to transform to the stable hexagonal form on account of sluggishness.

The method used in this investigation to obtain the oxygen solubility of solid cobalt at different temperatures seems particularly fitted for the reasonably accurate determination of this transformation temperature. Certainly the long exposures primarily undertaken to effect oxygen saturation at the different temperatures should carry this sluggish transformation to a definite end point, and the character of the results supports this anticipation.

It is believed that the specimens treated at 875° C. were at the transformation temperature within the experimental limit of temperature control. They did not attain an equilibrium oxygen content characteristic of either lattice but, probably owing to continual fluctuation of temperature, retained an oxygen content attributable to the presence of both lattices in some chance proportion.

The agreement between the transformation temperature derived from the discontinuity of the solid-solubility curve and the temperature deter-

mined by resistivity measurements with the pure metal is close enough to establish the fact of an equilibrium transformation temperature considerably below the values previously reported in the literature, with exception of the 850° C. value obtained by Cardwell<sup>3</sup>.

We believe that 850° C. is the best choice for the upper transformation temperature of pure cobalt, subject to the refinements of future experimentation, for the following reasons: We are confident that 875° C. is correct within the experimental error of about  $\pm 5^\circ$  C. for the reaction horizontal shown in Fig. 4. Therefore the transformation in the oxygen-free metal must be somewhat lower to meet the general requirements of the phase diagram shown, and a decrease of 25° C. would seem reasonable. Moreover, an earlier resistivity-temperature curve not reproduced here showed a sharp upper break at 850° C. Finally, the value selected agrees with the one contributed by Cardwell.

With respect to analogies between the closely related metals, iron, cobalt and nickel, it is interesting to reflect that with iron it is impossible to suppress the transformations except through alloying; in cobalt the transformations may be suppressed without difficulty, and in nickel, it is impossible not to suppress them, i.e., no transformations have been observed.

#### AN APPLICATION OF THE LAWS OF DILUTE SOLUTIONS

Fink and Freche<sup>13</sup> in a recent paper have shown that some of the laws of perfect solutions may be applied to aluminum-base binary alloys even outside of the range of dilute solutions. It is interesting to consider the equilibrium between cobalt and oxygen from this point of view.

From the principles of chemical thermodynamics, it can be shown that for ideal or very dilute solutions

$$\ln N_2 = \frac{\Delta H}{RT} + C,$$

where  $\ln N_2$  = natural logarithm of the mol fraction or atomic per cent of the pure solute.

$\Delta H$  = heat of crystallization or of precipitation.

$R$  = gas constant.

$T$  = absolute temperature.

$C$  = integration constant.

But  $R$  and  $C$  are constants and  $\Delta H$  is also nearly constant for a small change of temperature, so that this is the equation of a straight line with  $\ln N_2$ , or  $\log_{10} N_2$ , and  $\frac{1}{T}$  constituting the only variables. Therefore if  $\log_{10} N_2$  is plotted against  $\frac{1}{T}$ , a straight line must result if the

solution, liquid or solid, behaves ideally, and if the crystallizing or precipitating phase is a pure substance.

TABLE 2.—Data for Plotting  $\frac{1}{T}$  vs. Logarithm of Atomic Percentage of CoO

T° C.	T° K.	$\frac{1}{T_k}$	Oxygen, Per Cent	CoO, Per Cent	Atomic Per Cent CoO	Log. At. Per Cent CoO
600	873	0.00115	0.006	0.0281	0.0221	$\bar{2}.344$
700	973	0.00103	0.009	0.0421	0.0332	$\bar{2}.521$
810	1083	0.000925	0.016	0.0750	0.0588	$\bar{2}.769$
875	1148	0.000873	0.010	0.0468	0.0369	$\bar{2}.567$
945	1218	0.000822	0.007	0.0328	0.0258	$\bar{2}.412$
1000	1273	0.000787	0.008	0.0375	0.0295	$\bar{2}.470$
1200	1473	0.000680	0.013	0.0610	0.0479	$\bar{2}.680$

In applying this criterion to the behavior of oxygen in solid cobalt the data (see Table 2) were plotted as  $\frac{1}{T}$  vs. log. atomic per cent (mol

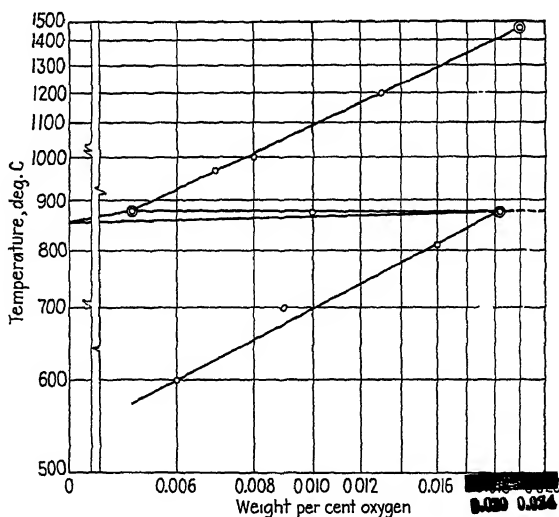


FIG. 6.—PHASE DIAGRAM FOR Co-CoO IN WHICH  $\frac{1}{T}$  IS PLOTTED AGAINST LOG OF ATOMIC PERCENTAGE CoO, BUT CENTIGRADE TEMPERATURES AND WEIGHT PERCENTAGES OF OXYGEN ARE SHOWN FOR COMPARISON WITH FIG. 4.

fraction) CoO. Both branches of the solid solution curve then became straight lines allowing for a small experimental error. However, in these very dilute solutions, the atomic percentage of dissolved substance is about the same whether it is calculated as CoO or O, so that the only real value of this analytical treatment of the data is to give assurance

that equilibrium must have been attained at each temperature of soaking, thus rationalizing the saturation limits shown in Table 1.

Fig. 6 shows the data plotted in the manner described except that the coordinates are made to read in degrees Centigrade and weight per cent of oxygen, after actually plotting  $\frac{1}{T}$  vs. log atomic per cent of CoO, so that a direct comparison may be made between Figs. 4 and 6.

As for the condition of the oxygen in these mixtures, Herty<sup>14</sup> has shown that oxygen must dissolve as FeO in liquid iron from similar considerations. If oxygen dissolves in this form in liquid iron it is not far afield to assume that it may dissolve as FeO in solid iron. Furthermore, Rhines and Mathewson<sup>1</sup> in their study of the copper-oxygen system found that cuprous oxide was lost from pure powdered compound and from the copper alloy, on heating in vacuo, by volatilization and decomposition in about the same ratio. This was taken as an indication that oxygen may be combined with copper in its migration through the copper lattice prior to volatilization. However, additional evidence is needed before it can be strongly argued that oxygen is dissolved in solid cobalt as CoO.

Since the points on the two branches of the line of solid solubility plotted in the manner described above fell quite well on straight lines certain points of special interest, indicated by double circles in Figs. 4 and 6, could be accurately located by extrapolation. This was desired because of the high temperature of soaking that would be required to carry out the experiment in one case, with probable attendant difficulties of proper temperature control; and in the other two cases, because the actual determination of points marking the extremities of the reaction horizontal would be a matter of considerable trial and error. It is believed that the points plotted in this manner, by extrapolation, result in a higher order of accuracy than could be achieved otherwise.

The upper extrapolation temperature was 1460° C., which undoubtedly is very close to the eutectic temperature. Questions affecting this and other aspects of the cobalt-oxygen system will be reported in another paper.

## SUMMARY

1. The solubility of oxygen in solid cobalt has been investigated through the range of temperature, 600° to 1500° C.
2. Evidence was discovered of a crystallographic transformation of cobalt in the cobalt-oxygen system at about 875° C.
3. This transformation was confirmed by electrical resistivity measurements of oxygen-free cobalt and was placed at 850° C. in the pure metal.

4. An expression based on the laws of dilute solutions was found to generalize the solubility data, thus offering good evidence that the experimental observations define a true condition of equilibrium.

5. A diagram of type summarizing the possibilities of equilibrium between Co and CoO in relation to pressure, temperature and concentration was presented to supply a theoretical foundation for the experimental method used.

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## A Study of the Molybdenum-carbon System

BY W. P. SYKES,\* MEMBER A.I.M.E., KENT R. VAN HORN,† MEMBER A.I.M.E., AND  
C. M. TUCKER†

RECENT investigations of the molybdenum-carbon alloys have been reported by Becker and Ebert<sup>1,‡</sup> Westgren and Phragmén<sup>2</sup>, T. Takei<sup>3</sup>, and H. Tutiya<sup>4</sup>. Takei<sup>3</sup> studied the Mo-C system by employing metallographic and X-ray methods, and the other publications described the determination of the crystal structure of the molybdenum carbides.

In exploring this system by a technique previously applied to the tungsten-carbon series<sup>5</sup>, the results of Takei were confirmed with two definite exceptions; i.e., first the composition of the eutectic, and second the nature of the carbon-rich intermediate phase. Consequently, a more thorough examination of the molybdenum-carbon constitution was initiated in an effort to correlate the data supplied by the microstructures, diffraction patterns and chemical analyses.

### METALLOGRAPHIC INVESTIGATION

A briquette of molybdenum powder when heated in a carburizing atmosphere at 1500° to 1600° C. for several hours develops the carbon-rich layer shown in Fig. 1. The carburization was accomplished by placing the briquette in a carbon tube, which was heated in the hydrogen atmosphere of an alundum muffle wound with tungsten resistor. While the macrostructure indicates two distinct shells, and suggests the possibility of two carbon-rich phases, no evidence of this condition could be detected by the microscope, which revealed but one high-carbon constituent. This carbide forms next to the molybdenum as a relatively dense, light-colored zone (Fig. 2) which passes abruptly into an outer layer of spongy texture. As will be noted later, only one intermediate phase was observed in the X-ray photograms prepared of different locations in the carburized zone. The metallographic structure at the inner border of the shell, reproduced in Fig. 3, shows a marked porosity accom-

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\* Metallurgist, Cleveland Wire Works, General Electric Co.

† Metallurgical Division, Aluminum Research Laboratories, Aluminum Company of America.

‡ References are at the end of the paper.



panying the formation of the carbon-rich constituent. This carbide was identified from the diffraction pattern as the  $\text{Mo}_2\text{C}$  solution, described by Westgren and Phragmén<sup>2</sup> and also by Takei<sup>3</sup>, having a homogeneity region between about 5.4 and 6.0 per cent carbon; it is termed  $\beta$  in the following discussion.

Specimens containing  $\beta$  were prepared by adding lampblack to molybdenum powder, thoroughly mixing and heating in a closed carbon container in hydrogen at 1500° to 1600° C. for 2 hr. The final carbon

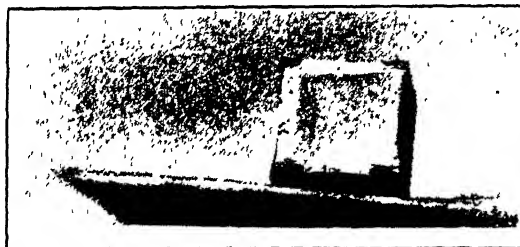


FIG. 1.—MOLYBDENUM CARBURIZED BY HEATING IN CARBON TUBE IN HYDROGEN ATMOSPHERE, AT 1500° TO 1600° C. FOR 10 HR.  $\times 2$ .

content was obtained by chemical analysis. This carburized material was then added to molybdenum powder in proper quantities to produce a series of alloys consisting of between 0.07 and 5.4 per cent carbon. The mixtures, after pressing into bars about  $\frac{3}{8}$  in. square, were again sintered in carbon at 1500° to 1600° C. for 2 hr. to approximate structural equilibrium in that temperature range. The composition of the bar was not altered by the final treatment below a depth of about 0.025 inch.

In the microstructure of a sample containing 0.09 per cent carbon no  $\beta$  was perceptible, but this phase appears in a considerable quantity when the carbon is increased to 0.21 per cent. The  $\beta$  is represented in Fig. 4 by the white areas, which resisted the 50 per cent  $\text{HNO}_3$  etchant. As in the tungsten-carbon system, the relatively high temperature of the solidus requires the use of a carbon resistor-crucible operated in a partial vacuum and for which the temperature-amperage relation had been determined<sup>5</sup>.

The solidus point was located by placing specimens of one composition which had received treatment at 1500°–1600° C. in the crucible and heating in 2 min. to a series of temperatures above 1600° C. until the microscope indicated liquid formation. This was detected after heating to  $2200^\circ \pm 25^\circ \text{C.}$  in the region between 0.21 and 5.4 per cent carbon.

The concentration of the  $\alpha$  molybdenum- $\beta$  eutectic was approximated as 1.8 per cent carbon by observations of the rate and extent of melting as well as the interior microstructures of specimens containing between

1.6 and 2.0 per cent carbon. These alloys were heated from 2000° to 2225° C. in 30 sec. and maintained at 2225° C. for 15 sec. Melting in the presence of carbon always results in the formation of a carbon-rich exterior. The nature of the inner liquid portion, however, affords positive evidence as to the eutectic composition. Fig. 5 illustrates a slight amount

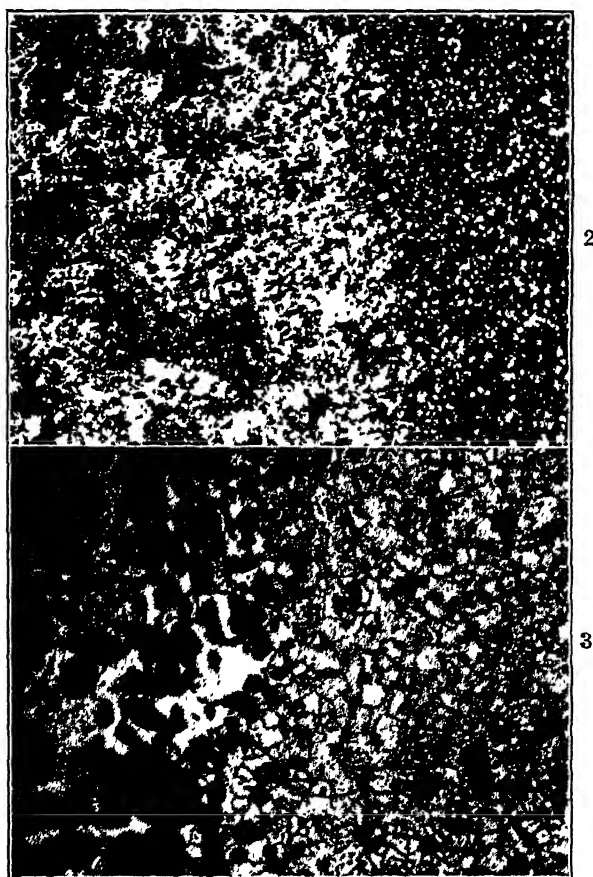


FIG. 2.—MOLYBDENUM CARBURIZED AS IN FIG. 1. SURFACE SHELL OF CARBIDE AT LEFT, MOLYBDENUM SOLUTION AT RIGHT.  $\times 100$ .

FIG. 3.—MOLYBDENUM CARBURIZED AS IN FIG. 1. JUNCTION OF CARBIDE (LEFT) AND MOLYBDENUM SOLUTION (RIGHT).  $\times 500$ .

All microsections etched with 50 per cent nitric acid.

of excess  $\beta$  surrounded by a eutectic structure in a 2 per cent carbon sample. Two sections of completely fused material from which the carbon-rich surface layer had been removed analyzed 1.73 and 1.92 per cent carbon. These specimens before melting consisted of 1.62 per cent carbon. This eutectic concentration is appreciably different from the value of 4 per cent carbon estimated by Takei<sup>3</sup>.

As the carbon approaches 5.4 per cent, the quantity of liquid existing at 2200° C. decreases. The microstructure of a sample containing

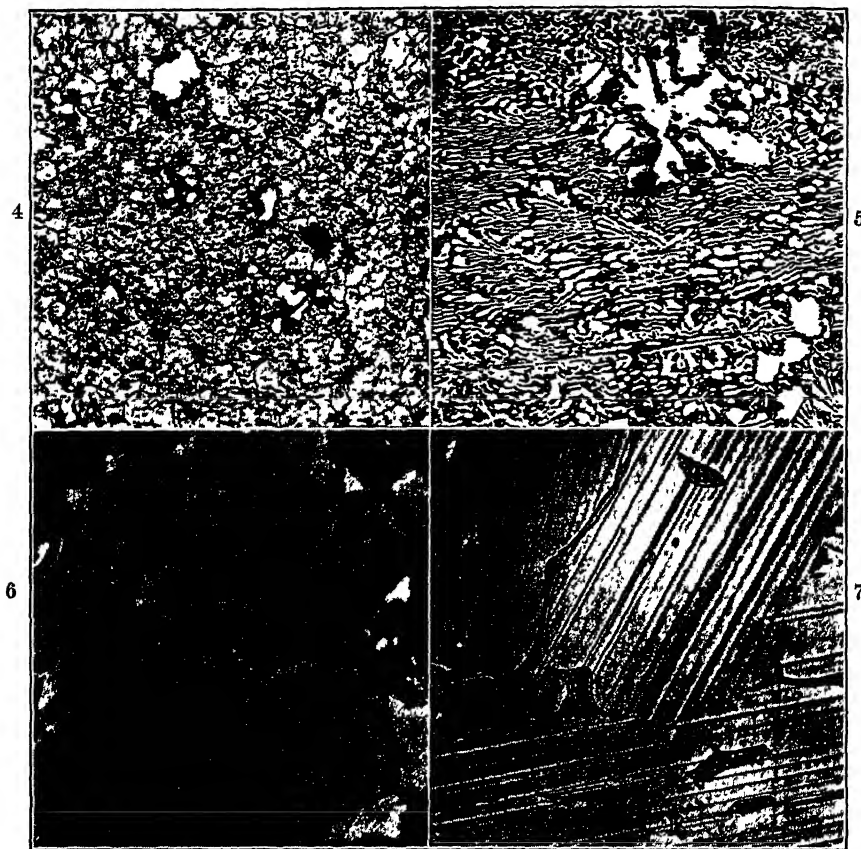


FIG. 4.—MOLYBDENUM CONTAINING 0.21 PER CENT CARBON ADDED AS  $\text{Mo}_2\text{C}$  ( $\beta$ ). SINTERED AT 1500° TO 1600° C. FOR 2 HR. EXCESS  $\beta$  APPEARS AS LIGHT CONSTITUENT.  $\times 500$ .

FIG. 5.—MOLYBDENUM CONTAINING 2 PER CENT CARBON, MELTED AT 2200 C.° IN CARBON CRUCIBLE.  $\times 200$ .

FIG. 6.—MOLYBDENUM WITH 5.36 PER CENT CARBON ADDED. SINTERED 2 HR. AT 1500 TO 1600° C., THEN HEATED AT 2200° C. FOR 5 MIN.  $\times 500$ .

FIG. 7.—MOLYBDENUM CONTAINING 5.36 PER CENT CARBON. TREATED AS SPECIMEN OF FIG. 6, THEN REHEATED AT 2450° C. FOR 2 MIN. AND COOLED TO 2100° C. IN ABOUT 1 MIN.  $\times 500$ .

Lenses of eutectic appear in matrix of striated  $\beta$ .

5.36 per cent carbon after heating at 2200°  $\pm$  25° C., which is represented in Fig. 6, reveals the unmelted  $\beta$  enclosed by a network of eutectic. This same composition (5.36 per cent carbon), when heated to 2450° C. and cooled slowly to below the solidus, freezes with a structure shown in

Fig. 7. The striations in the  $\beta$  phase are always evident when the alloy has been cooled from appreciably above to below the solidus and suggests a precipitation in the  $\beta$ .

Between 6 and 10 per cent carbon, liquid occurs first on heating to  $2400^{\circ} \pm 50^{\circ} \text{C}$ . As the carbon content exceeds 6 per cent, the structure of the solidified metal assumes the form reproduced in Fig. 8. A new constituent ( $\gamma$ ) appears as a black lustrous crystal with the striated  $\beta$  phase. The  $\gamma$  becomes more abundant as the carbon increases to about 10 per cent and is shown in two types in Fig. 9. In this specimen (10.25

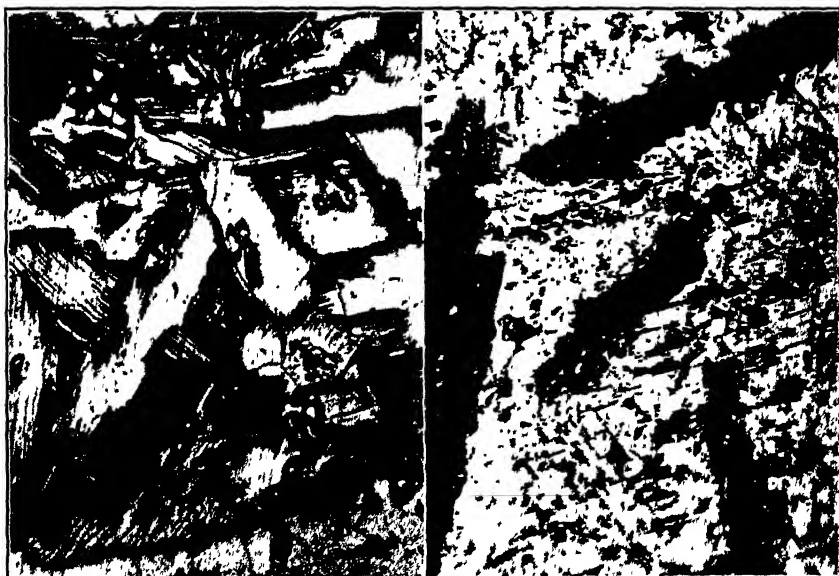


FIG. 8.—MOLYBDENUM CONTAINING 7.2 PER CENT CARBON. FUSED BY HEATING IN CARBON CRUCIBLE AT  $2500^{\circ} \text{C}$ . FOR 2 MIN.  $\times 200$ .

Striated crystals of  $\beta$  formed from melt on cooling.

FIG. 9.—MOLYBDENUM WITH 10.25 PER CENT CARBON ADDED. PARTIALLY MELTED AT  $2750^{\circ} \text{C}$ .  $\times 200$ .

Black constituent  $\gamma$  appears to occur both as a primary crystal and as a precipitate from solid  $\beta$ .

per cent carbon) which had been thoroughly fused by heating at  $2750^{\circ} \text{C}$ ., massive  $\gamma$  crystals appear to have solidified from the liquid. In addition, a pronounced Widmanstätten pattern has developed in the  $\beta$ , which seems to consist of small angular  $\gamma$  particles. The  $\gamma$  crystals (see Fig. 10) are hard, distinctly brittle and are easily removed from the metallic matrix. A chemical analysis of two samples of this constituent, mechanically isolated from the surrounding metal, determined the composition to be 12.3 and 13.0 per cent carbon. The concentration of this material before partial melting at  $2750^{\circ} \text{C}$ . was 10.25 per cent carbon. An X-ray film was also procured of the separated  $\gamma$ , which will be described.

When the carbon content of the sintered alloys is less than about 6 per cent, occasionally about 0.2 per cent free carbon has been detected chemically. As the carbon is increased above 6 per cent, the combined carbon of the sintered material remains approximately constant at 5.7 to 5.9 per cent, the excess occurring as free carbon. This suggests that the treatment at 1500° to 1600° C. is effective in producing the  $\beta$  phase but is not conducive to the formation of  $\gamma$ . The latter carbide, however, forms



FIG. 10.—CRYSTALS OF PRIMARY  $\gamma$  REMOVED FROM 10.25 PER CENT MOLYBDENUM-CARBON ALLOY AFTER PARTIAL FUSION AT 2750° C.  $\times 100$ .

readily at temperatures above 2400° C., probably as the product of the indicated peritectic reaction. Takei<sup>3</sup> regarded the  $\gamma$  phase as graphite, which is very improbable considering the present data.

#### PREPARATION OF SAMPLES AND DIFFRACTION METHODS

The majority of alloys prepared for the experiments were in the form of small blocks which had been pressed, sintered and reheated to the desired heat-treating temperatures. The samples were quenched from the final heating or sintering temperatures, ground, polished and deeply etched to remove the distorted exterior zone prior to the metallographic and X-ray examination. Diffraction photograms were produced by the wedge method of reflecting from the polished surface of the small blocks. This procedure avoided the inaccuracies due to specimen size and variation in penetration, characteristic of powder analysis, and permitted the additional advantage of utilizing solid samples. The reflection cassette containing a  $\text{ZrO}_2$  filter was designed so that a sodium chloride standard could be simultaneously exposed and the resulting pattern recorded on the film adjacent to that of the material to be investigated. Only three alloys, a 0.05 per cent carbon mixture, a 5.36 per cent carbon specimen (Mo-C-1), and a mechanically isolated intermediate phase, were powdered, screened, and examined by the Debye-Hull method. The powder was placed in one part of a Pyrex glass capillary

1 mm. outside diameter, then a separating cotton plug and finally sodium chloride were inserted in the remaining section. The capillary was sealed at the extremities and centered on a camera containing a  $ZrO_2$  filter.

Powder and reflection photographs were obtained on a General Electric multiple diffraction apparatus equipped with a molybdenum-target water-cooled tube operating at about 30 kv. and 20 ma. The exposure periods with Eastman Diaphax films were 48 hr. In measuring the positions of the reflections, corrections were applied for any dimensional change in the film by reference to the sodium chloride standard included on each pattern. The intensities of the various lines were appraised and segregated in five classes.

### DISCUSSION OF RESULTS

The photographs of the different alloys established the existence of two intermediate phases in addition to the molybdenum solid solution ( $\alpha$ ) in the range of 0 to 10.25 per cent carbon. The composition of the samples, method of preparation and heat-treatments that produced only the body-centered  $\alpha$  solution are compiled in Table 1, while Tables 2 and 3 respectively summarize the conditions of forming the carbides  $\beta$  and  $\gamma$ , which may occur separately or with the adjacent constituent.

TABLE 1.—*Method of Preparation and Treatment of Molybdenum-carbon Alloys Containing only Molybdenum Solid Solution  $\alpha$  as Determined by Diffraction Analysis*

Specimen No.	Carbon, Per Cent	Method of Preparation or Sintering Treatment	Final Sintering or Heating Temp., Deg. C.	Time at Temperature	Remarks
Mo-C-19	0.05	Mixture of molybdenum and $Mo_2C$ powder to give 0.05 per cent carbon.			No Mo C detected
Mo-C-15-2	0.07	Molybdenum powder carburized by heating in carbon tube in hydrogen. Pressed.	1500–1600	4 hr.	No $Mo_2C$ detected

The data incorporated in Tables 1 and 2 show that the molybdenum-rich intermediate phase  $\beta$  was not detected until 0.09 per cent carbon had been added to molybdenum. A film of specimen Mo-C-15-2 (0.07 per cent C.) heated at 1500° to 1600° C. revealed only  $\alpha$  molybdenum solution reflections. Consequently, the X-ray results indicate that the solid solubility of carbon in molybdenum is between 0.07 and 0.09 per cent at temperatures from 1500° to 2100° C. T. Takei<sup>3</sup> previously proposed an

approximately constant solubility limit of 0.3 per cent carbon from room temperature to 1800° C.

TABLE 2.—*Method of Preparation and Treatment of Molybdenum-carbon Alloys Containing Molybdenum-rich Phase  $\beta$  ( $\text{Mo}_2\text{C}$ ) as Determined by Diffraction Analysis*

Specimen No.	Carbon, Per Cent	Preparation and Sintering Treatment	Final Sintering or Heating Temp., Deg. C.	Time at Temperature	Relative Quantity of Phases
Mo-C-11-B	0 09	Mo-C-1 added to Mo powder, pressed and sintered in carbon tube for 2 hr. at 1500°-1600° C. Reheated in carbon crucible in vacuum.	2000-2110	5 min.	Very small $\beta$ Matrix $\alpha$
Mo-C-3-A	0 21	Mo-C-1 added to Mo powder, pressed and sintered in carbon tube in hydrogen	1500-1600	2 hr.	Small $\beta$ Matrix $\alpha$
Mo-C-3-2	0 21	Mo-C-3-A reheated in carbon crucible in vacuum.	2000-2100	5 min.	Small $\beta$ Matrix $\alpha$
Mo-C-9-2	3 0	Mo-C-1 added to Mo powder, pressed and sintered 1500°-1600° C. for 2 hr. in carbon tube in hydrogen. Reheated in carbon crucible in vacuum.	2000-2100	5 min.	Very large $\beta$ Large $\alpha$
Mo-C-14-A	4 0	Mo-C-1 added to Mo powder, pressed and sintered in carbon tube in hydrogen.	1500-1600	2 hr.	Very large Medium $\alpha$
Mo-C-14-B	4 0	Mo-C-14-A reheated in carbon crucible in vacuum.	2000-2100	5 min.	Very large $\beta$ Medium $\alpha$
Mo-C-14-C	4 0	Mo-C-14-B reheated in carbon crucible in vacuum.	2000-2300	1 min.	Very large $\beta$ Medium $\alpha$
Mo-C-2-B	4 85	Pressed and sintered in carbon tube in hydrogen at 1500°-1600° C. for 2 hr. Reheated in carbon crucible in vacuum.	2000-2100	5 min.	Very large $\beta$ Very small $\alpha$
Mo-C-1	5 36	Prepared by mixing lampblack and Mo powder, heating in carbon tube in hydrogen.	1400	15 hr.	Entirely $\beta$
Mo-C-1-B	5 36	Mo-C-1 pressed and sintered in carbon tube in hydrogen for 2 hr. at 1500°-1600° C. Reheated in carbon crucible in vacuum.	2000-2100	5 min	Entirely $\beta$
Mo-C-1-C	5 36	Mo-C-1-B reheated in carbon tube in hydrogen.	1550	3 hr.	Entirely $\beta$
Mo-C-23-A	5 7	Heated at 2000°-2200° C. for 10 min. Reheated in carbon crucible in vacuum.	2300	5 min.	Entirely $\beta$
Mo-C-23-B	5.7	Mo-C-23-A reheated in carbon tube in hydrogen.	1550	3 hr.	Entirely $\beta$
Mo-C-17-A	5 75 combined (10.25 total)	Heated in carbon crucible in vacuum.	2000-2200	10 min.	Entirely $\beta$
Mo-C-17-B	5 75 combined (10.25 total)	Heated from 2000° to 2450° C. in 5 min. in carbon crucible in vacuum.	2450	1 min.	Very large $\beta$ Trace $\gamma$
Mo-C-17-C	5 75 combined (10.25 total)	Mo-C-17-B reheated in carbon tube in hydrogen.	1550	3 hr.	Entirely $\beta$
Mo-C-17-D	12 3	10 25 per cent carbon added to molybdenum. Heated in carbon crucible in vacuum from 2000° to 2750° C. in 3 min., then at 2750° C. for 1 min. Black crystals isolated from matrix.			Sm Very large $\gamma$
Mo-C-16-A	5.96 combined (6.30 total)	Heated in carbon tube in hydrogen.	1500-1600	35 hr.	Entirely $\beta$
Mo-C-18-A	5.96 combined (6.33 total)	Heated in carbon crucible in vacuum.	2000-2100	10 min.	Entirely $\beta$
Mo-C-18B	5.96 combined	Mo-C-18-A reheated in carbon tube in hydrogen.	1550	3 hr.	Entirely $\beta$
Mo-C-6	7 20	Mo powder and lampblack mixed and heated in carbon tube in hydrogen.	1400	15 hr.	Large $\beta$ Trace $\gamma$

The molybdenum-carbon samples, listed in Table 1, consisting of the  $\alpha$  solid solution, exclusively exhibited a decrease in the unit cell dimen-

sions of the element molybdenum. The body-centered  $\alpha$  pattern was associated with that of the carbide  $\beta$  in photograms of alloys containing from 0.09 to 4.85 per cent carbon (Table 2), the former diminishing in intensity with increasing carbon. In all films, the  $\alpha$  solution lines registered a lattice contraction dependent on the carbon content. The molybdenum parameter of  $3.140 \pm 0.004\text{\AA}$ ., ascribed by Neuberger, was reduced to  $3.108 \pm 0.004\text{\AA}$ . (about a 1 per cent contraction) by the dispersion of smaller carbon atoms, inferring that the  $\alpha$  solution is of the simple substitution type.

TABLE 3.—*Method of Preparation and Treatment of Molybdenum-carbon Alloys Containing High-carbon Phase  $\gamma$  as Determined by Diffraction Analysis*

Specimen No.	Carbon, Per Cent	Method of Preparation and Sintering Treatment	Final Sintering or Heating Temp., Deg. C.	Time at Temperature	Relative Quantity of Phases
Mo-C-17-B	5.75	Heated in carbon crucible in vacuum from 2000° to 2450° C. in 5 minutes.	2450	1 min.	Very large $\beta$
Mo-C-6	7.20	Mo powder and lampblack mixed, heated in carbon tube in hydrogen.	1400	15 hr.	Trace $\gamma$ Large $\beta$
Mo-C-6-A-2	7.20	Mo-C-6 pressed and heated in carbon crucible in vacuum.	2100-2300	5 min.	Trace $\gamma$ Very large $\gamma$
Mo-C-17-D	12.3	10.25 per cent carbon added to molybdenum. Heated in carbon crucible in vacuum from 2000° to 2750° C. in 3 min., then at 2750° C. for 1 min. Black crystals isolated from matrix.			Trace $\beta$ Very large $\gamma$ Small $\beta$

The intermediate high-molybdenum phase  $\beta$  was encountered in all specimens containing over 0.09 per cent carbon (Tables 2 and 3). In the composition range of 0.09 to 4.85 per cent carbon, samples heated from 1500° to 2300° C. produced patterns of both  $\beta$  and the  $\alpha$  molybdenum solution, representing a two-phase region which microscopically was observed to consist of primary  $\alpha$  and the  $\alpha$ - $\beta$  eutectic, from 0.09 to 1.8, and primary  $\beta$  and  $\alpha$ - $\beta$  eutectic, from 1.8 to between 4.85 and 5.36 per cent carbon.

In 10 alloys containing from 5.36 to 5.96 per cent carbon heated at various temperatures from 1400° to 2400° C. (Table 2) and below the solidus, only the molybdenum-rich carbide  $\beta$  could be detected. Therefore, the single-phase  $\beta$  field extends at 1400° to 2400° C. from about 5.36 to 5.96 per cent carbon and includes the composition 5.88 per cent carbon corresponding to the formula  $\text{Mo}_2\text{C}$ . The constituent described as  $\beta$  was previously identified by Westgren and Phragmén<sup>2</sup>, Takei<sup>3</sup>, and Tutiya<sup>4</sup> as  $\text{Mo}_2\text{C}$ , having a hexagonal close-packed



atomic arrangement. The first two researches employed iron radiation and Tutiya used copper and molybdenum anticathodes. The various functions of the diffraction angles of the crystallographic planes favorably

TABLE 4.—*Diffraction Measurements of Molybdenum-rich Intermediate Phase  $\beta$ ,  $\text{Mo}_2\text{C}$  Solid Solution*

Author		Takei	Tutiya	Westgren and Phragmén	Westgren and Phragmén	Sykes, Van Horn and Tucker	Sykes, Van Horn and Tucker
Composition		5.5 Per Cent C	5.8 Per Cent C (?)	4.63 Per Cent C	7.4 Per Cent C	5.36 Per Cent C Heated at 1500°-1600° C	4 Per Cent C Heated at 1500°-1600° C.
Miller Indices	Intensities	Interplanar Spacings, Ångstroms					
100	Strong		2.594	2.597	2.60	2.59	2.53
002	Strong		2.364	2.37	2.365	2.36	2.31
101	Very strong	2.275	2.273	2.282	2.285	2.27	2.23
102	Strong	1.745	1.745	1.75	1.75	1.75	1.723
110	Strong	1.496	1.495	1.496	1.50	1.50	1.481
103	Strong	1.344	1.345	1.345	1.35	1.35	1.334
112	Strong	1.265	1.264	1.266	1.267	1.269	1.256
201	Strong	1.247	1.249	1.25	1.25	1.254	1.242
004	Weak		1.18	1.181	1.181	1.183	1.174
202	Weak	1.137	1.136	1.136	1.14	1.139	1.131
104	Weak	1.074	1.075	1.075	1.075	1.08	1.069
203	Medium		1.00	1.00	1.002	1.003	0.990
211	Medium	0.958	0.95	0.957	0.963	0.962	0.957

TABLE 5.—*Close-packed Hexagonal Lattice Dimensions of Molybdenum-rich Intermediate Phase  $\beta$ ,  $\text{Mo}_2\text{C}$  Solid Solution*

Investigators	Composition, Per Cent C.	Ångstroms		
		$a_1$	$a_2$	$\frac{a_2}{a_1}$
Takei.....	5.5	2.995	4.723	1.576
Tutiya.....	5.8(?)	2.994	4.722	1.577
Westgren and Phragmén .....	5.08	2.993	4.725	1.579
Westgren and Phragmén .....	7.4	3.004	4.725	1.573
Sykes, Van Horn and Tucker ...	5.36	3.001	4.723	1.573
Sykes, Van Horn and Tucker . . . . .	4.0	2.960	4.620	1.560

oriented for reflection obtained by the different foreign investigators were converted to interplanar spacings  $d$  and incorporated in Table 4. In Table 5 the hexagonal parameters of  $\beta$  are summarized. The agreement of the results is indeed remarkable. Measurements from the

present study of specimen Mo-C-1 (5.36 per cent carbon heated at 1400° C. for 15 hr.), composed of  $\beta$  of similar lattice dimensions, are also listed.

Westgren and Phragmén<sup>2</sup> and also Takei<sup>3</sup> discovered that the  $\beta$  carbide had an appreciable solubility or homogeneity range extending from 5.5 to 6 per cent carbon, which closely approximates the limits defined in the preceding paragraph. It was observed that the interplanar spacings of  $\beta$  were markedly smaller for alloys containing from 3 to 4.85 than for samples consisting of from 5.36 to 5.96 per cent carbon, indicating that carbon expanded the hexagonal close-packed unit cell. Data for specimen Mo-C-14-A (4 per cent carbon heated at 1500° to 1600° C. for 2 hr.) which suffered a large contraction compared to the lattice of the high carbon Mo-C-1, is recorded in the last column of Table 4. The increase in parameter with the introduction of carbon atoms suggests that the  $\beta$  or Mo<sub>2</sub>C solution is of the interstitial or additive type similar to the dispersion of carbon in gamma iron or iron in tungsten.

The existence of a carbon-rich intermediate phase has not been generally recognized, as Takei<sup>3</sup>, who made the only effort to investigate the Mo-C constitution, concluded that above 6 per cent carbon Mo<sub>2</sub>C solution and graphite occur, with the latter predominating in higher carbon alloys. Westgren and Phragmén<sup>2</sup> noted weak, unexplained reflections on the photogram of a 7.4 per cent carbon sample but did not ascertain whether the origin was a high-temperature Mo-C constituent or oxidized impurities. Westgren<sup>2</sup> intimated that the symmetry of the additional lines could not have been derived from a composition represented by the formula MoC, analogous to the phase WC. Recently, however, H. Tutiya<sup>4</sup>, in determining the crystal structure of the molybdenum carbides, prepared a specimen supposedly corresponding to the stoichiometric ratio MoC (11.1 per cent C) having a hexagonal close-packed atomic arrangement of appreciably different lattice dimensions than Mo<sub>2</sub>C.

When an alloy containing 5.75 per cent carbon is heated above 2400° C. (this composition from 1400° to 2400° C. is comprised entirely of  $\beta$ ), or when the carbon content exceeds 6 per cent, a new constituent appears, which has been called  $\gamma$ , the carbon-rich intermediate phase. The patterns of the two carbides  $\beta$  and  $\gamma$  are somewhat similar because of the coincidence of a number of reflections, but, on careful inspection, could be easily differentiated. The sample, Mo-C-17-B (5.75 per cent C), heated at 2450° C. for one minute, consisted of a large quantity of  $\beta$  and a trace of  $\gamma$ , and on subsequent heating at 2750° C. (Mo-C-17-D, 5.75 per cent C), the proportion of the two components is reversed. The presence of  $\gamma$  at 2450° C. confirms the microscopic observation of the 2400° C. peritectic temperature,  $\beta \rightleftharpoons \gamma + \text{melt}$ . When the carbon exceeds 6 per cent, the quantity of  $\gamma$  is increased and that of  $\beta$  diminished until at 10 per cent carbon, the former phase is the principal constituent.

The interplanar spacings and intensities of the important diffracting planes of the carbide  $\gamma$  and similar data for Tutiya's "MoC"<sup>4</sup> are compiled in Table 6. The absence of coincident lines is obvious and indicates that the reflections did not originate from the same phase. Chemical analysis of  $\gamma$  crystals mechanically separated from a 10.25 per cent carbon specimen gave values of 12.3 and 13.0 per cent carbon, which represents the composition of part of the homogeneity range of the high carbon  $\gamma$  which is adjacent to the molybdenum-rich carbide  $\beta$  of the Mo-C system. It is also possible that the  $\gamma$  single-phase field may include the concentration 11.1 per cent carbon (MoC).

TABLE 6.—*Diffraction Measurements of High-carbon Intermediate Phase  $\gamma$  and Tutiya's "MoC"*

Miller Indices	Tutiya's "MoC"		Carbon-rich Intermediate Phase, Observed in 7.20 Per Cent C. Alloy Heated to 2100°–2300° C.	
	Intensities	Interplanar Spacings, Å.	Intensities	Interplanar Spacings, Å.
001	Strong	2.785	Weak	2.54
100	Very strong	2.510	Medium	2.50
101	Very strong	1.865	Strong	2.39
110	Strong	1.45	Very strong	2.245
002	Very Weak	1.392	Strong	2.07
111	Strong	1.286	Weak	1.91
200	Weak	1.256	Weak	1.604
102	Medium	1.218	Strong	1.486
201	Medium	1.145	Weak medium	1.361
112	Medium	1.005	Strong	1.266
210	Weak	0.95	Weak	1.246
202	Weak	0.933	Weak medium	1.214
			Weak	1.053
			Weak	1.029
			Weak	1.009

The briquette of molybdenum powder heated in a carburizing atmosphere at 1500° to 1600° C., illustrated in Fig. 1, was examined. Patterns were obtained from the dark, spongy surface, the bright inner shell, and the core. The interpretation revealed that the two exterior layers were similar, consisting of only the molybdenum-rich carbide  $\beta$  (no evidence of  $\gamma$ ), and of course the adjacent interior was  $\alpha$  molybdenum solution, substantiating the microscopic analysis. A similar treatment of tungsten would produce the high-carbon phase exterior WC, a tungsten-rich W<sub>2</sub>C intermediate shell, and a tungsten core. Apparently the carbide  $\gamma$  of the Mo-C system is not formed at 1500° to 1600° C., but only at higher temperatures, which is consistent with the conditions of preparation of the samples where  $\gamma$  has been detected by X-ray methods (Table 3).

A tentative constitutional diagram of the molybdenum-carbon system (Fig. 11) has been constructed from the data previously published and that presented in the preceding pages. It is believed that this embodies all the information thus far available.

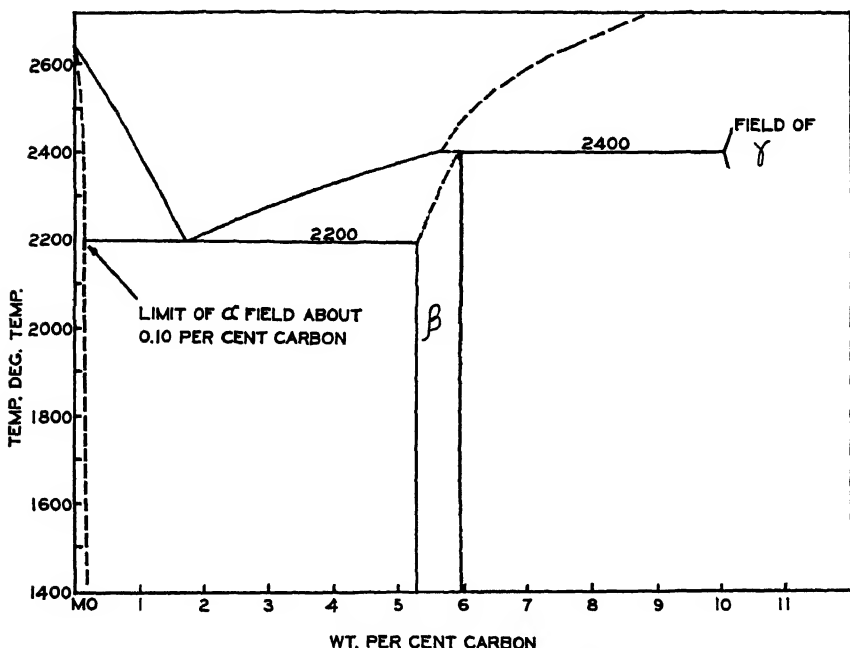


FIG. 11.—TENTATIVE CONSTITUTIONAL DIAGRAM OF MOLYBDENUM-RICH END OF MOLYBDENUM-CARBON SYSTEM.

#### SUMMARY OF PHASES OF THE MOLYBDENUM-CARBON SYSTEM

The  $\alpha$  molybdenum solution and two intermediate phases, the molybdenum-rich  $\beta$  and the high-carbon  $\gamma$ , were encountered in the portion of the Mo-C system investigated.

The  $\alpha$  molybdenum solution extends to 0.09 per cent carbon in the range 1500° to 2100° C. indicating the limit of solubility of the carbon atoms that are dispersed (substitution type) in the body-centered lattice.

The single-phase field of the molybdenum-rich carbide  $\beta$  or  $\text{Mo}_2\text{C}$  solution has been more definitely defined occurring from about 5 to 6 per cent carbon between 1400° and 2400° C. The hexagonal close-packed lattice is expanded by the interstitial introduction of carbon atoms in the  $\beta$  homogeneity region.

The high-carbon intermediate phase  $\gamma$  was observed in 5.36 per cent carbon specimens heated above 2450° C. and predominated in higher carbon alloys. Isolated crystals analyzed 12.3 and 13.0 per cent carbon, indicating the composition of a portion of the  $\gamma$  solubility range.

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## DISCUSSION

(Samuel L. Hoyt presiding)

S. L. HOYT,\* Milwaukee, Wis. (written discussion).—The writer's interest in the field of metal carbides has been confined largely to tungsten carbide, though to some extent it has related to the subject matter of the present paper. In the Annual Lecture before the Institute of Metals Division in 1930 (TRANSACTIONS, vol. 89) both of the phases MoC and Mo<sub>2</sub>C were mentioned. It was pointed out that the identity of the monocarbide was in doubt, but lattice parameters were given of a hexagonal close-packed phase that presumably was MoC. The authors have compared their own work with that of Tutiya, which had not as yet appeared when the lecture was given. It would be interesting to have the comparison extended to the parameters reported, which were  $a = 4.88$  and  $c/a = 1.34$ . We thought that this phase was most likely the MoC but did not have sufficient data for positively identifying it. The authors find a discrepancy between their work and that of Tutiya. It might help to clarify this situation if the authors were to include the above data in their table and show which one they most closely resemble.

The work reported by the authors on the phase Mo<sub>2</sub>C agrees with our findings, which were also reported in the lecture.

Another point seems to be worth mentioning; that is, the nomenclature adopted for the intermediate phases of alloy systems. Should we use Greek letters or formulas for compounds? If the latter, the naming of phases that are identifiable as compounds becomes greatly simplified. If the phase is an intermediate solid solution with no compound for a base, the Greek letter could be used with propriety. Here the system that has been started by Westgren appears to be the most logical and correct one to use. According to it, all homologous phases with similar atomic arrangement and constitution are given the same letter. This is a tremendously useful system in its field. The Mo-C system is a third one, because the compounds dissolve one or the other of the components and the intermediate phase occurs over a range of composition. Here I think we should use the name that has the greater significance, and if possible make it fit Westgren's system. In the present instance it would appear preferable to use the formulas instead of Greek letters.

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\* Research Metallurgist, A. O. Smith Corporation.

C. S. SMITH,\* Waterbury, Conn.—Regarding the terminology of alloys, I believe that crystallographers are causing some confusion by loosely adopting the name of a phase in the first system examined containing a particular structure as the name of a *phase* in other systems instead of as a name for the *structure*. It is usual to refer, for example, to  $\text{Cu}_2\text{S}$  as having the fluorite structure, but this does not mean that it is fluorite, which is practically what is implied when all phases with a structure like gamma brass, for example, are called gamma. The distinction should be made between phases of gamma-brass structure and phases that are called gamma by the metallurgists, for some other but well established reason.

However, I do believe that the names of phases should indicate their structure and should like to see an attempt made to establish an internationally acceptable system of nomenclature, based on structure and applicable to both phases and structures but using a new set of terms and symbols, which are not already names in extensive use by the metallurgist.

The metallurgist's present system is defective, since it requires a name to be changed whenever a new phase is found in a given system, is inapplicable to ternary systems, and is subject to arbitrary selection as to which end of the system to start from. The establishment of a system of nomenclature based upon structure but applicable as names for both phases and structures would obviate all difficulty, and it is highly desirable that such a system be set up. The use of terms already in extensive use with a precise meaning should be avoided.

J. T. NORRON,† Cambridge, Mass. (written discussion).—The authors state that the formation of an alpha solid solution of carbon in molybdenum is accompanied by a decrease in the parameter of the molybdenum of about one per cent (3.140 to 3.108 Å.). This corresponds to about 0.08 per cent carbon. This is very surprising, for one would expect the formation of an interstitial solid solution, as in iron, since both are transition elements. This situation is always accompanied by an increase in parameter. If the solid solution is truly a substitution one in which a carbon atom replaces a molybdenum atom, the decrease in parameter should be about 10 per cent, which is what the authors find.

The beta compound in this system has a typical interstitial structure and this is generally believed to be derived from interstitial alpha solid solutions in which what is in effect an overcrowding of the metalloid atoms has caused the metal atoms to rearrange. With the exception of iron, not many of these alpha solutions have been examined with care and, perhaps, if this is done, using the high precision that is now possible with X-rays, some new information will be obtained.

H. A. SCHWARTZ,‡ Cleveland, Ohio (written discussion).—The phase that the authors designate as beta is referred to on the second page of the paper as the  $\text{Mo}_2\text{C}$  solution. From the location in the proposed constitutional diagram in Fig. 11 of the homogeneous beta field between the two-phased fields, alpha-beta and beta-gamma, it would seem probable that beta, which is by observation of variable composition, is a homogeneous solid solution of the alpha and gamma phases. If this is so, it is likely that there will be some variation of solubility with temperature and that the boundaries of beta are not two parallel vertical lines but that these lines have some slight inclination to the vertical too small to have been recognized experimentally and perhaps too small to have been visible on the scale of the diagram.

There would seem to be some possible question whether the right-hand boundary of the beta field corresponding rather closely to the formula  $\text{Mo}_2\text{C}$  has the significance

\* Research Metallurgist, American Brass Co.

† Associate Professor, Physics and Metals, Massachusetts Institute of Technology.

‡ Manager of Research, National Malleable & Steel Castings Co.

of a chemical compound or merely represents the limit of solubility of gamma in alpha that happens to fall near the composition of this compound; or, if the right-hand boundary of the present beta field is taken as representing a true compound, beta would seem to be a solid solution of alpha in that compound and there would then be requisite some sort of an area, however narrow, to the right of the composition  $\text{Mo}_2\text{C}$  representing the solubility of gamma in that carbide.

This writer ventures the preceding comments mainly because his interest in the molecular constitution of solid solutions is much greater than his knowledge thereof.

J. T. NORTON.—It is very surprising that in a structure of this sort, where there is a combination of a transition metal such as molybdenum, with a small metalloid atom such as carbon, we should find a carbon atom replacing a molybdenum atom in the lattice. It would be interesting if this is true, and we have no reason to doubt it, based on the information of the authors. If it is confirmed, we may have to change our ideas a little.

The only question I have to raise is the question of the iron solid solution, and the real reason we think that alpha iron forms an interstitial solution is that the parameter is increased. We know that by diffraction measurements. If a substitutional solid solution were formed, a decrease would be found. I think that is the principal basis for the idea that carbon forms an interstitial solid solution in iron. It is also true that the beta, or the phase of this system that has been designated as beta, must be of an interstitial type. It is very strange to me to find that the alpha solution behaves in another way.

W. P. SYKES, K. R. VAN HORN AND C. M. TUCKER (written discussion).—The authors have noted the agreement of the parameters of  $\beta$ , the  $\text{Mo}_2\text{C}$  solid solution, with those described by Dr. Hoyt in the annual Institute of Metals lecture in 1930. In regard to the high-carbon phase  $\gamma$ , the present paper listed different values than those found by Tutiya for MoC. Tutiya claimed MoC to have a hexagonal cell,  $a = 2.91\text{\AA}$ ,  $c = 2.786\text{\AA}$ ,  $c/a = 0.968\text{\AA}$ ; Dr. Hoyt reported in the lecture a hexagonal cell of  $a = 4.88\text{\AA}$ ,  $c = 6.54\text{\AA}$ ,  $c/a = 1.34\text{\AA}$ , on the basis of measurements by T. A. Wilson. These values do not resemble Tutiya's, nor do the present authors'. Unfortunately it will not be possible at this time to answer Dr. Hoyt's second question regarding a comparison of his parameters of MoC and those of the high-carbon intermediate phase,  $\gamma$  of the present paper. A preliminary survey of the diffraction measurements indicated that the  $\gamma$  phase is probably not hexagonal or of simple crystal structure. It is hoped that future work will identify the spatial relations of the atoms of the constituent described as  $\gamma$ , having an appreciable homogeneity range.

It is also probable that naming of the intermediate phases of the Mo-C system after the simple stoichiometric ratio of the components which is included in the homogeneity range of each of the intermediate solid solutions ( $\text{Mo}_2\text{C}$  and MoC) would have been more significant than the Greek letters. Dr. Hoyt's remarks on the terminology of the intermediate phases and Dr. Smith's reply to these remarks are pertinent. Certainly a name or symbol related to the atomic arrangement of the various phases would be desirable and assist in predicting the occurrence of new phases in different systems. However, when the metallographic name of the phase in the first system that is investigated is adopted to represent a certain crystal structure type, the method of naming all homologous phases with similar atomic arrangement is not as effective as would be if some consideration were given to naming the first crystal type encountered. Also where the crystal types occur frequently, only a few terms are necessary, but many systems will have individual phases of different crystal structure and would require additional symbols. In the progress of time with more accurate and detailed investigations, if all the phases were named with symbols according to their structure there would certainly be a voluminous list of names.

With the present metallographic method of naming the intermediate phases alpha, beta, gamma, etc., from the base metal, a single system does not have a great number of phases and the same terms may be similarly used for another system, although the terms have no crystallographic significance.

Dr. Norton's comments on the type of solution of carbon in molybdenum are interesting. We were pleased to know that the calculated effect of substituting carbon for molybdenum in the molybdenum lattice, at the limit of solid solubility, agreed with the observed. It would appear, therefore, that the substitutional type is definite, and that the system Mo-C is probably an exception to Professor Westgren's analogies of the interstitial alpha solid solutions formed by the transition elements (Fe, Mo, Co, etc.). The exception seems more unusual because the intermediate phase richest in molybdenum ( $\beta$ ) is a solution of the interstitial type, the parameter increasing in dimensions with the addition of carbon. The intermediate phases having a solubility range in which the added metal is interstitially dispersed are generally derived from interstitial solutions of the base metal.

In regard to Dr. H. A. Schwartz's comments,  $\beta$  is a definite intermediate phase of variable composition. It is not a solid solution of the  $\alpha$  and  $\gamma$  phases as it has an entirely different structure from either  $\alpha$  or  $\gamma$  and actually is a solution of carbon in  $\beta$ . However, the boundaries of the  $\alpha$ - $\beta$  and  $\beta$ - $\gamma$  region may be inclined rather than parallel, indicating a change in solubility with temperature, but this was not detectable with the methods employed.

The right-hand extremity of the  $\beta$  field closely approximates the composition of the compound,  $\text{Mo}_2\text{C}$ . This boundary does not represent the solubility of  $\alpha$  in  $\gamma$ , but represents the solubility of carbon in  $\beta$ .  $\beta$  is an intermediate phase of variable composition and since the composition  $\text{Mo}_2\text{C}$  occurs in the homogeneity range may be termed  $\text{Mo}_2\text{C}$  solid solution (which seems more significant to Dr. Hoyt). The composition  $\text{Mo}_2\text{C}$  may approximately limit the solution of carbon in  $\beta$  but does not indicate a definite compound susceptible to the solution of both molybdenum and carbon, because carbon expands the  $\beta$  lattice from 5.36 to 5.96 per cent carbon and an increase in molybdenum in this range should cause a contraction of the lattice which would be impossible because of the size of the molybdenum atom. Unfortunately, we were not able to prepare alloys containing more than 5.96 per cent carbon and could not exactly determine whether more than this quantity would dissolve in  $\beta$ . However, the composition 5.96 per cent carbon is greater than that represented by the formula  $\text{Mo}_2\text{C}$ , or 5.88 per cent carbon, so that this value does not apparently limit the solubility of carbon in  $\beta$ .



## Equilibrium Relations in the Copper Corner of the Ternary System Copper-tin-beryllium\*

BY ELBERT S. ROWLAND† AND CLAIR UPTEGROVE‡, MEMBER A.I.M.E.

(New York Meeting, February, 1935)

THE widespread interest in the alloys of beryllium with copper is due principally to the fact that certain compositions show very favorable precipitation-hardening characteristics and are, in fact, the strongest nonferrous alloys known at the present time. Investigations have been conducted by Masing and Dahl and others on the physical characteristics of ternary beryllium alloys, in an attempt to produce precipitation-hardening effects with a smaller amount of beryllium than that required in the binary copper-beryllium alloys (2.0 to 2.5 per cent Be). The results of these investigations show that ternary alloys of beryllium with Cu-Sn, Cu-Al and Cu-Zn, among others, exhibit promising improvements in physical properties after precipitation-hardening treatment and, while the increases in properties obtained are not as high as those realized from the binary copper-beryllium alloys, excellent properties are obtained with beryllium contents averaging about one-half the amount required in the binary alloys.

This paper presents the results of an investigation of the equilibrium relations of certain alloys containing copper, tin and beryllium. The alpha-phase boundary of the ternary system is given for alloys containing from 0 to 1 per cent beryllium. The equilibrium conditions beyond the alpha-phase boundary are presented for alloys containing up to 32 per cent tin and 1 per cent beryllium. The data were collected by means of quenching experiments, microscopic examination and thermal analysis. The results of some powder-method X-ray determinations on the alloys, conducted by Mr. William Mikulas and Prof. Lars Thomassen at the University of Michigan, are used as evidence in this paper. The com-

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† Instructor in Mineral Technology, The Pennsylvania State College, State College, Pa.

‡ Professor of Metallurgical Engineering, University of Michigan, Ann Arbor, Mich.

plete findings of their X-ray investigations will be published as a separate paper.

## REVIEW OF THE LITERATURE

*Copper-tin System.*—Since the literature on this system has been thoroughly covered in several recent papers by other authors, a review of the great amount of work done will not be attempted. It is sufficient to say here that parts of the diagram are in a very controversial state and that the different investigators are not in agreement on the interpretation of several important transformations in this system.

*Copper-beryllium System.*—The first investigation into the equilibrium relations in this system was carried out by Oosterheld<sup>1</sup>\* in 1916. He identified four phases in the range from 0 to 18 per cent beryllium. The alpha phase was found to be a solid solution of beryllium in copper and to extend from 0 to 1.6 per cent beryllium, the boundary being vertical. Beta was indicated as a solid solution which underwent a eutectoid inversion into alpha and gamma from 1.6 to about 11.6 per cent beryllium, the eutectoid point being at 6 per cent and 580° C. Gamma was described as a solid solution with a solubility range of from about 11.5 to 12.8 per cent beryllium. Delta appeared above 12.8 per cent beryllium.

Corson<sup>2</sup> in 1926 and Bassett<sup>3</sup> in 1927 independently investigated the mechanical properties of several alloys in this system. Corson decided that the alpha-phase boundary occurred at 1.9 per cent beryllium. Both of these investigators, as well as Oosterheld, failed to investigate the possibility of precipitation-hardening.

Masing and Dahl<sup>4</sup> were the first to publish a diagram of this system that showed a decreasing alpha-phase solubility with decreasing temperature. The alpha-phase boundary was found to decrease from 2.8 per cent at the peritectic temperature (865° C.) to 1.72 per cent at the eutectoid temperature (578° C.) and finally to 0.75 per cent beryllium at 400° C.

In 1932, Borchers<sup>5</sup> published the results of a quite complete study of the copper-beryllium system up to 33 per cent beryllium. The greater portion of his diagram is reproduced in Fig. 1. It was arrived at by means of thermal, dilatometric, micrographic and electrical methods. He succeeded in clearing up the very complicated liquidus and solidus situation over the beta field, originally reported by Oosterheld, but the rest of his diagram differs very little from the one reported by Masing and Dahl.

Dahl, Holm and Masing<sup>6</sup> reported on X-ray structure determinations on some of the phases in this system in 1929. They found that the face-

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\* References are at the end of the paper.

centered cubic lattice of copper contracts progressively to a maximum of about 3 per cent by the addition of beryllium, the supersaturated alpha phase with 2.5 per cent beryllium having a lattice parameter of 3.564Å. The gamma phase was found to have a body-centered cubic lattice of the caesium chloride type with a parameter of 2.70Å. They

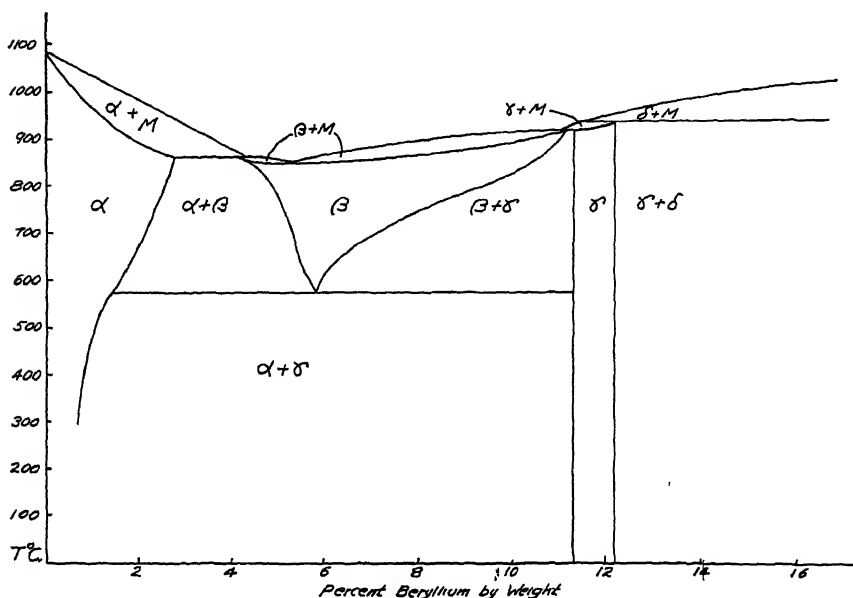


FIG. 1.—THE COPPER-BERYLLIUM SYSTEM. (Borchers.)

concluded that this phase was the compound CuBe, although a range of solubility was indicated. They also found that the delta phase had a hexagonal close-packed structure but did not determine the parameters. They were unable to obtain any data on the beta phase.

Tanimura and Wassermann<sup>7</sup> reported on an X-ray determination of the alpha-phase solubility in 1933 and found a larger decrease in solubility with decrease in temperature than any previous investigators. They reported the alpha-phase boundary to occur at 2.1 per cent beryllium at the peritectic temperature, 1.8 per cent at 700°, 0.4 per cent at 400° and at about 0.16 per cent at 250° C.

*The Ternary System.*—The only previously published work on the copper-tin-beryllium system was carried out by Masing and Dahl<sup>8</sup> in 1929, while determining whether these alloys were amenable to a precipitation-hardening treatment. They determined the alpha-phase solubility at 750° C. by microscopic examination of eight quenched alloys, which had been previously annealed for one hour at that temperature. They found that the boundary of the ternary alpha region

in the ternary diagram was approximately determined by the straight composition line of the binary boundary concentrations at that temperature. Their annealing time was undoubtedly too short to produce equilibrium in the alloys.

### PROCEDURE

The metals used in preparing the alloys for this investigation were electrolytic copper (99.96 per cent Cu), Baker's C.P. tin and a copper-beryllium master alloy, analyzing 12.4 per cent beryllium, which was kindly furnished by the Beryllium Products Corporation. An Ajax-Northrup induction furnace was used to prepare 500-gram melts, the alloys being melted in a graphite crucible under a covering of powdered graphite. In addition, an atmosphere of hydrogen was used to guard against oxidation until all of the metal had melted and had disappeared under the graphite blanket. The entire copper charge was melted as rapidly as possible and superheated to 1370° C. (2500° F.), when the copper-beryllium master alloy was added piece by piece, each addition being held under the surface until it had dissolved. Care was taken to prevent the temperature of the melt from falling below 1340° C. (2450° F.), as it was found that the rate of solution of the master alloy below 1340° C. was too slow to prevent oxidation of beryllium before solution was completed. The temperature was then lowered, the tin added, the heat held for adjustment of pouring temperature (about 10 min.) and then poured into a tapered, hexagonal graphite mold, previously heated to about 300° C. Temperatures were read by means of a calibrated Leeds & Northrup optical pyrometer.

The heats listed in Table 1 were all given a preliminary anneal of 48 hr. at temperatures ranging between 650° and 700° C., depending upon the composition. A number of ingots were selected at random and checked for segregation from top to bottom and edge to center by microscopic methods. In no case was any segregation observed.

Several ingots from each constant beryllium group were analyzed and their analyses checked the calculated composition within very close limits. (See Table 1.) Beryllium was determined by extracting both copper and tin from a sulfate solution in a mercury cathode, precipitating  $\text{Be}(\text{OH})_2$  from the resulting solution with a small excess of  $\text{NH}_4\text{OH}$ , igniting the precipitate and weighing as  $\text{BeO}$ . Copper was determined electrolytically in the presence of both tin and beryllium by the method proposed by Etheridge<sup>9</sup> and later modified by Hammond<sup>10</sup>. Tin was determined on the filtrate by a modification of the method of Etheridge.

The annealing furnace and method of heat treatment were patterned after those used by Eash and Uptegrove<sup>11</sup> in a previous equilibrium investigation. In place of the copper block, the samples were annealed

TABLE 1.—*Composition of Alloys Investigated*

Heat No	Composition by Weight, Per Cent			Atomic Composition, Per Cent		
	Be	Sn	Cu	Be	Sn	Cu
1	0.25	10 0	89 75	1.82	5.53	92.65
2	0.25	11 0	88 75	1 83	6 11	92.06
3	0.25	12 0	87 75	1 84	6.71	91 45
4	0.24 <sup>a</sup>	13 0	86.73 <sup>a</sup>	1 85	7.30	90 85
5	0.25	14 0	85 75	1.85	7 89	90 26
6	0.25	15 0	84 75	1 86	8 51	89 63
7	0.25	18 0	81 75	1.89	10 38	87 63
8	0.27 <sup>a</sup>	20 0	79 75	1 91	11.63	86 46
9	0 25	22 0	77 75	1.93	12.92	85 15
10	0.23 <sup>a</sup>	24 0	75 75	1 95	14 32	83 82
11	0 25	26 0	73 75	1.97	15.59	82 44
12	0.25	28 0	71 75	1.99	16.95	81.06
13	0.24 <sup>a</sup>	30.0	69 71 <sup>a</sup>	2 01	18.38	79 61
14	0.25	32.0	67.75	2.04	19 88	78 08
15	0 5	1.0	98 5	3 44	0 52	96 04
16	0.5	3 0	96 5	3 47	1.50	94 95
17	0 5	5.0	94 5	3.50	2 66	93.84
18	0 49 <sup>a</sup>	6 09 <sup>a</sup>	93 45 <sup>a</sup>	3.52	3.21	93 27
19	0.5	7.0	92 5	3 54	3 76	92 70
20	0.5	9.0	90 5	3 56	4 88	91 56
21	0.5	10 0	89 5	3 58	5.45	90 97
22	0 5	11 0	88 5	3 60	6 03	90 37
23	0.5	13 0	86 5	3 64	7 18	89 18
24	0 5	15 0	84 5	3 67	8.35	87 98
25	0.47 <sup>a</sup>	17 0	82.49 <sup>a</sup>	3 70	9 59	86.71
26	0.5	19.0	80.5	3.74	10 80	85 46
27	0.5	21 0	78 5	3.78	12.08	84 14
28	0.50 <sup>a</sup>	23.0	76.47 <sup>a</sup>	3 82	13.35	82 83
29	0.5	25 0	74.5	3.86	14 67	81 47
30	0.5	27.0	72.5	3.89	15 98	80 13
31	0.5	29.0	70.5	3 93	17.35	78.72
32	0.48 <sup>a</sup>	31 0	68.5	3 97	18.72	77 31
33	1.0	1 0	98 0	6 68	0.5	92 82
34	1.0	2 0	97 0	6 71	1.02	92 27
35	1.01 <sup>a</sup>	3 00 <sup>a</sup>	95 94 <sup>a</sup>	6 74	1 54	91.72
36	1.03 <sup>a</sup>	4 0	95.0	6 77	2.06	91 17
37	1.0	5.0	94 0	6 80	2 58	90 62
38	1.0	5 5	93 5	6 82	2 85	90.33
39	1.0	6 0	93.0	6 83	3 12	90 05
40	1.0	6 5	92 5	6 85	3 39	89.76
41	1 0	7.0	92 0	6 86	3 66	89 48
42	1 01 <sup>a</sup>	8.0	91 0	6 89	4 20	88 91
43	0.98 <sup>a</sup>	9 0	90 03 <sup>a</sup>	6 92	4.73	88.35
44	1 0	11 0	88 0	6 99	5 85	87 16
45	0 99 <sup>a</sup>	13 0	85 97 <sup>a</sup>	7.04	6 95	86.00
46	1 0	15 0	84 0	7 12	8 12	84.76
47	1.0	17.0	82 0	7 18	9 29	83 53
48	1 0	19 0	80 0	7 25	10.49	82 26
49	1.0	21 0	78 0	7.32	11 69	80.99
50	1 0	23 0	76 0	7 39	12.93	79 68
51	1 01 <sup>a</sup>	25.0	74 0	7 46	14 20	78.34
52	1 0	27 0	72 0	7 53	15 47	77.0
53	1 0	28 5	70 5	7 59	16 45	75 96
54	0 98 <sup>a</sup>	30 0	69 0	7.65	17.47	74 88

<sup>a</sup> Composition by chemical analysis.

in a nickel-chromium-iron heat-resistant block, which just fitted inside the D-shaped muffle of the electric furnace. This annealing block (4 by 5 by 10 in.) was cast with six 1-in. diameter holes extending back from one face to a depth of 8 in. The furnace temperature was maintained by an automatic controller and was held to a  $\pm 2^\circ$  C. variation during the annealing period. Temperature gradients within the block, controlled by means of a heating element in the door, were always less than  $2^\circ$  C. Newly calibrated thermocouples were inserted in the block for each annealing treatment. Later on in the investigation, another furnace of smaller size but identical in design and operation was built to expedite the work.

Small samples weighing about 5 grams each were cut from the lower portion of the ingots, so that each sample represented one-half the cross-section of the ingot. The samples to be quenched from each temperature were placed in separate closed-end Monel metal tubes, which were fitted into the holes in the annealing block. The temperature of the furnace was raised to between  $680^\circ$  and  $760^\circ$  C. (depending upon the solidus point of the alloys) and maintained for a period of 7 days (168 hr.). The tube containing the samples to be quenched from a given temperature was removed and the samples immediately immersed in water at  $0^\circ$  C. The furnace temperature was then slowly and uniformly lowered to the next desired quenching temperature and maintained there for 48 hr. The tube containing the samples to be quenched at that temperature was then removed and the samples quenched. This procedure was repeated until all the samples had been quenched. In this way, over 400 samples were treated, the total annealing time of the samples used for microscopic investigation ranging from 168 to over 500 hr. in some cases.

Nearly all of the alloys investigated were found to be remarkably resistant to oxidation in air. In a qualitative way, oxidation resistance was found to increase rapidly with increase in beryllium content. Except for the very low tin, 0.25 per cent beryllium alloys, the amount of oxide produced during the annealing treatment was only enough to darken the surface slightly. It is hoped that some quantitative measurements can be made on these alloys in the future.

The quenched samples were ground, polished and etched with alcoholic ferric chloride, this reagent proving the most satisfactory. The results of the microscopic investigation are plotted in the diagrams reproduced herein.

Liquidus and solidus temperatures of 33 alloys were obtained by means of inverse-rate thermal analysis. A vertical tube furnace containing the crucible, 150-gram melts and a calibrated Pt-PtRh thermocouple were used in making the measurements. The couple was connected to a type K precision potentiometer and the data obtained with two stop watches in the usual manner. Cooling and heating rates of between

2° and 3° C. per minute were maintained. The transformation temperatures plotted in the diagrams were obtained by averaging the points recorded on heating and cooling.

In order to obtain more accurate results on the position of the solidus over the alpha phase than could be obtained by thermal analysis, this boundary was determined by 1-hr. annealing treatments on about 24 samples, followed by quenching and microscopic examination. These experiments were conducted at 20° C. temperature intervals for each composition tested until a sample was obtained that showed grain-boundary melting.

Inverse-rate thermal analyses were conducted on 21 alloys to determine certain solid state transformations within closer limits than could be conveniently done by quenching experiments. Samples  $\frac{3}{4}$  in. long and  $\frac{1}{2}$  in. in diameter were machined or ground from the ingots and a small hole drilled in one end to accommodate a noble metal thermocouple. The sample and couple were enclosed in a closed-end protection tube, which was supported in a vertical electric tube furnace. The transformation points were obtained by the method used on melting points.

### THE BINARY SYSTEMS

No work was done on either the copper-tin or copper-beryllium systems. The work of Borchers<sup>5</sup> was accepted as a basis for the copper-beryllium side of the ternary diagram. The work of Tanimura and Wassermann<sup>7</sup> on the alpha-phase boundary would seem to require some confirmation before acceptance.

Certain portions of the copper-tin equilibrium diagram are in such a controversial state at the present time that any critical comparison of the various proposed diagrams is exceedingly difficult, if not impossible. With numerous interpretations possible for different parts, it would be expected that the results obtained in a study of the ternary system would not conform completely to the conditions set up in any one proposed copper-tin binary diagram, but might show good agreement with certain portions of individual diagrams. In the work done by Eash and Upthegrove<sup>11</sup> on the ternary system copper-tin-nickel, confirmation was seemingly found for Stockdale's<sup>12</sup> alpha-solubility determination, for Carsons'<sup>13</sup> gamma range and Bauer and Vollenbruck's<sup>14</sup> transformation from beta to gamma. Further confirmation of the alpha-phase boundary as drawn by Stockdale and the Carson gamma boundary was obtained by quenching experiments on copper-tin binary alloys by Eash and Upthegrove.

The results of the present study of the ternary system in which beryllium is the third element are again found to conform to the conditions set up by Stockdale's solubility determinations and Carson's gamma

region. Evidence for the extension into the ternary system of the  $590^{\circ}$  transformation ( $\alpha + \beta$  field) of the binary system, is present but direct support for a step mechanism appears lacking, although no concerted attempt was made to prove or disprove this latter point. The results on the ternary system show a general conformance to the conditions set up in Carson's binary diagram for alloys containing more than 16 per cent tin. Beryllium present to 0.25 per cent or more also appears to favor the extension of the  $590^{\circ}$  transformation across the  $\beta$  field, as indicated in the binary Cu-Sn diagram proposed by Hama-sumi and Nishigori<sup>15</sup>.

It is perhaps significant that the results obtained by Eash and Upthegrove on the copper-tin-nickel system and the present authors on the copper-tin-beryllium system, while conforming to the same conditions for the binary system in certain ranges of composition, do not conform for intermediate concentrations, particularly those involving the  $\beta$  to  $\beta'$  and  $\gamma$  transformations. This is especially significant when considered in connection with the variations in this portion of the diagrams of recent investigators of the binary system. As pointed out by Stockdale and others, some of the copper-tin phases are extremely unstable and the difficulty of fixing them by quenching is very great. It appears that certain elements such as nickel retard these transformations (particularly the  $590^{\circ}$  transformation) very greatly while other elements, such as beryllium, have little effect. It is possible that similar effects may be obtained with small amounts of other elements. If so, small amounts of impurities may have played an important part in the widely varying interpretations of the copper-tin diagram.

## RESULTS OF THE INVESTIGATION

In view of the complexity of the equilibrium relations in the ternary system, it was thought advisable to approach it from the standpoint of quasibinary sections of constant beryllium content by weight. Hence, quasibinary sections containing 0.25, 0.50 and 1.0 per cent beryllium by weight and varying amounts of tin up to 32 per cent were investigated.

*The 0.25 Per Cent Beryllium Copper-tin System.*—The diagram of the 0.25 per cent beryllium quasibinary section is given in Fig. 2. It shows that this beryllium concentration is entirely within the solid solubility of beryllium in the copper-tin alloys and the diagram therefore appears as a modified form of the binary diagram. The introduction of an extra degree of freedom causes the major portion of the modification.

The  $\alpha$  solubility increases with decreasing temperature from 11.8 per cent tin at  $784^{\circ}$  C. to 12.8 per cent at  $562^{\circ}$  C. With the appearance of  $\delta$ , however, the  $\alpha$ -phase solubility decreases, the minimum occurring at about 10.8 per cent tin at  $300^{\circ}$  C. When this solubility is



only slightly exceeded, delta appears as small blue angular particles in the tan alpha matrix (Fig. 3). This type of structure undoubtedly is due to precipitation of the delta from the alpha on cooling.

Fig. 4 shows the darker beta, which is readily recognizable from the lighter alpha. Many attempts were made with the 0.25 per cent beryl-

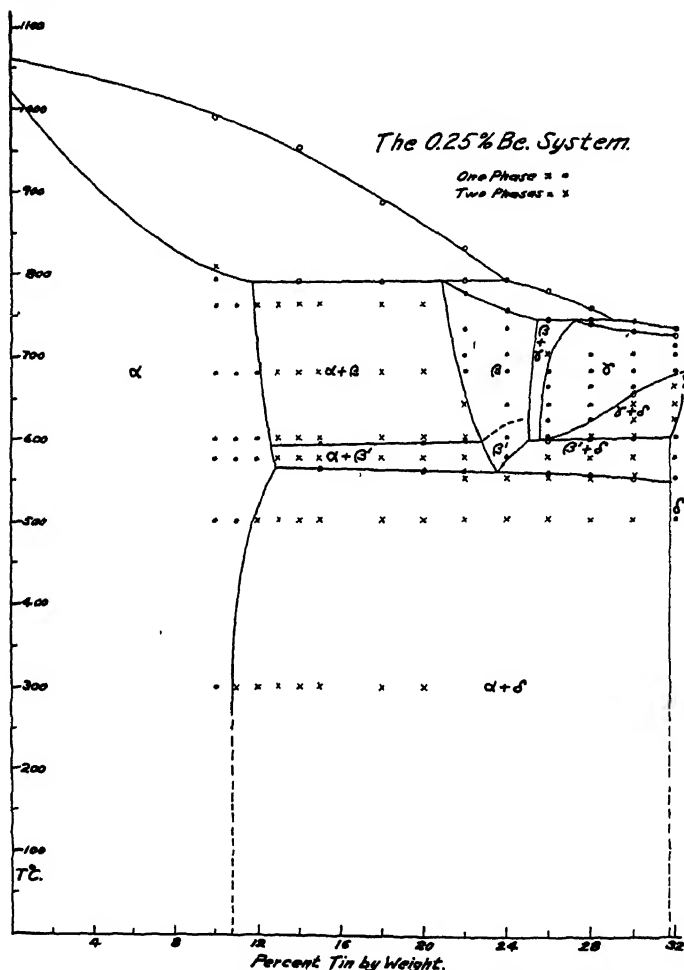


FIG. 2.—THE 0.25 PER CENT BERYLLIUM COPPER-TIN SYSTEM.

lium and other ternary alloys to produce the well-known striated or martensitic form of the beta phase. In all cases the beta remained free from striations or other markings, the beryllium apparently preventing the appearance of this form of beta.

Thermal analysis on alloys between 15 and 22 per cent tin showed small but definite and reproducible arrests at temperatures ranging between 589° at 15 per cent tin and 593° at 22 per cent tin. When long

annealing times were employed, no microscopic evidence of this transformation could be obtained. A 20 per cent tin alloy quenched from  $760^{\circ}$  (Fig. 4) was not microscopically different from a 22 per cent tin alloy quenched from  $575^{\circ}$  (Fig. 5), except for a slight difference in the amount of alpha present. There seemed a possibility, however, that the failure to obtain any evidence of a reaction rim might be associated with the very long annealing periods and slow rates of cooling employed when passing through this temperature zone. Consequently, a series of the alloys was annealed for 200 hr. at  $700^{\circ}$  C. and then slowly cooled ( $0.5^{\circ}$  C. per min.) to the temperature range of the transformation, and quenched. The result with the 18 per cent tin alloy, quenched from  $591^{\circ}$  (Fig. 6) is a definite, though small, reaction rim. Other samples of this composition cooled in the same way and quenched from above and below this temperature failed to show a reaction rim. The appearance of the rim in the sample cooled steadily and then quenched from the transformation zone and not from below it, or when annealed for long periods of time, is in agreement with the experience of other investigators attempting to produce Hoyt's beta transformation. The results again point to the existence of an intermediate phase between the beta and the eutectoid transformation at about  $560^{\circ}$  C. The microscopic evidence also shows that the transformation occurs rapidly and that, in the regular annealing procedure, it was completed long before the end of the time used (48 hr.). Hence, no microscopic evidence of the change was obtained from samples at or near equilibrium below the temperature of the transformation. This change in the beta phase was indicated as rising across the beta field, following the results of Hamasumi and Nishigori<sup>15</sup> on the binary copper-tin system, although no experimental evidence was obtained of this change in the beta field of this quasibinary section.

The nature of the  $590^{\circ}$  C. transformation constitutes one of the very much debated and still unsolved questions of the copper-tin system. In the present ternary study, it has appeared desirable to designate the phase intermediate between beta and the eutectoid formation as beta prime, the eutectoidal decomposition of this phase into alpha + delta occurring in the 0.25 per cent beryllium quasibinary section at 23.5 per cent tin. Successive samples of the 24 per cent tin alloy were quenched at various temperatures from  $730^{\circ}$  to  $575^{\circ}$  C. (48 hr. minimum annealing time at each quenching temperature) without any change in structure being observed. The gamma phase, which had a structure readily distinguishable from beta, did not occur with less than 25 per cent tin at any temperature. These results seem to preclude the possibility of the alpha + delta eutectoid being the result of decomposition of the gamma phase. The temperature of the eutectoid transformation, as determined by thermal analysis, decreases gradually with tin content. Figs. 7 and 8 show the structure of this very stable eutectoid in the presence of alpha.



FIGS. 3-8.—CAPTIONS ON OPPOSITE PAGE.



FIG. 9.—26 PER CENT SN, 0.25 PER CENT BE. QUENCHED AT 700° C. BETA + GAMMA (SPOTTED).  $\times 250$ .

FIG. 10.—28 PER CENT SN, 0.25 PER CENT BE. QUENCHED AT 680° C. GAMMA.  $\times 250$ .

FIG. 11.—28 PER CENT SN, 0.25 PER CENT BE. QUENCHED AT 600° C. GAMMA (SPOTTED) + DELTA.  $\times 250$ .

FIG. 12.—28 PER CENT SN, 0.25 PER CENT BE. QUENCHED AT 575° C. BETA PRIME + DELTA (IN RELIEF).  $\times 250$ .

FIG. 3.—12 PER CENT SN, 0.25 PER CENT BE. QUENCHED AT 300° C. ALPHA + DELTA.  $\times 250$ .

FIG. 4.—20 PER CENT SN, 0.25 PER CENT BE. QUENCHED AT 760° C. ALPHA (LIGHT) + BETA.  $\times 250$ .

FIG. 5.—22 PER CENT SN, 0.25 PER CENT BE. QUENCHED AT 575° C. ALPHA (LIGHT) + BETA PRIME.  $\times 250$ .

FIG. 6.—18 PER CENT SN, 0.25 PER CENT BE. SLOWLY COOLED AFTER 200 HR. AT 700° C. TO 591° C. AND QUENCHED.  $\times 250$ .

FIG. 7.—15 PER CENT SN, 0.25 PER CENT BE. QUENCHED AT 300° C. ALPHA + DELTA.  $\times 250$ .

FIG. 8.—22 PER CENT SN, 0.25 PER CENT BE. QUENCHED AT 500° C. ALPHA + DELTA.  $\times 250$ .

The numerous delta particles in the alpha areas of Fig. 7 are due to precipitation from the alpha and not to a break-up of the eutectoidal areas.

Only one sample was obtained in the beta + gamma area of this diagram but sufficient samples of a like nature were obtained in other quasibinary sections to definitely place this sample as beta + gamma

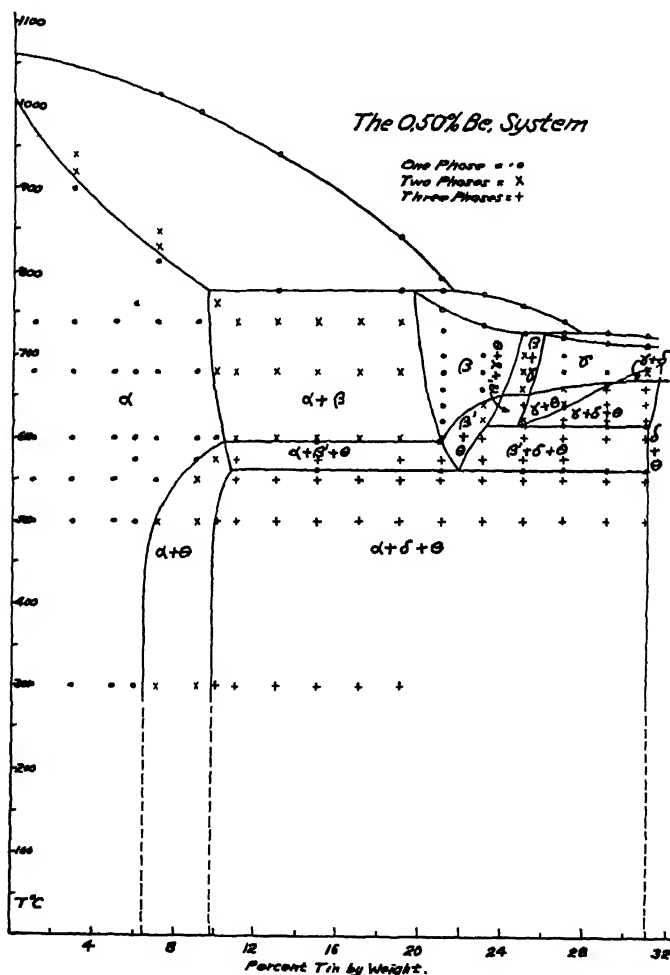


FIG. 13.—THE 0.50 PER CENT BERYLLIUM COPPER-TIN SYSTEM.

(Fig. 9). The gamma phase, wherever observed, was found to be pink in color (white light) and to be so unstable that even the most rapid rates of quenching failed to prevent some decomposition in the form of small, dark blue spots. This decomposition, found to be irregular over the sample, increases rapidly with tin content. This instability of the gamma phase is not peculiar to these ternary alloys, since many

investigators have noticed it in the binary copper-tin alloys. Fig. 10 shows a representative gamma structure in which the decomposition is marked.

Alloys containing 28 per cent or more of tin showed the presence of delta associated with gamma when quenched from within the triangular area marked gamma + delta in Fig. 2. The gamma phase decomposed as usual but the decomposition was less marked than in the pure gamma



FIG. 14.

FIG. 15.

FIG. 14.—9 PER CENT SN, 0.50 PER CENT BE. QUENCHED AT 300° C. ALPHA + THETA.  $\times 1000$ .

FIG. 15.—19 PER CENT SN, 0.50 PER CENT BE. QUENCHED AT 575° C. ALPHA (LIGHT) + BETA PRIME + THETA (WHITE WITH BLACK BOUNDARIES).  $\times 250$ .

area. The delta phase was easily identified by its clear blue color. The decomposition of gamma is believed to be due to the separation of finely dispersed delta during quenching. If the quench could be made drastic enough, the delta soluble in the gamma at the quenching temperature would be retained. This decomposition does not in any way affect the relative amounts of the two phases in the gamma + delta region since sufficient time was not allowed during quenching for appreciable diffusion to occur. Fig. 11 shows a representative structure in the gamma + delta field.

The investigators of the binary copper-tin alloys have ascribed the formation of a beta (beta prime) + delta region to either a peritectoid reaction between beta or gamma and eta to produce delta (Bauer and Vollenbruck<sup>14</sup>, Raper<sup>16</sup>, Matsuda<sup>17</sup>, etc.) or a eutectoid inversion of gamma into beta and delta (Corey<sup>18</sup>, Carson<sup>13</sup>, etc.). In the ternary alloys of copper, tin and beryllium, the formation of the beta prime + delta region appears to be the result of a eutectoid inversion of the gamma phase. The presence of this eutectoid transformation was indicated by thermal analysis and microscopic examination, the presence of a gamma + delta area above the transformation temperature precluding the

possibility of the change being of peritectoidal character. The intensity of the heat effect, as estimated from inverse-rate curves, showed a definite decrease as the tin content increased from 26 to 30 per cent. The beta prime phase, present below the eutectoid, was easily distinguished microscopically from gamma, present above the inversion, by reason of the difference in color and the freedom of the beta prime phase from decomposition. The character of the change is shown in Fig. 11, a 28 per cent tin sample quenched from 600° C., and Fig. 12, another sample of the same composition but quenched from 575° C. The lighter delta portions of Fig. 12 show the partial coalescence of the eutectoid with the long annealing time employed.

No evidence was obtained concerning the exact temperature of the crystallization of delta from gamma but consideration of the slope of the boundaries of the gamma + delta field, obtained principally from quenching experiments, placed it at about 680° and 32.5 per cent tin. No attempt was made to determine the high-tin boundary of the delta phase, but a definite solubility range was indicated from the results on the 32 per cent tin alloy.

*The 0.50 Per Cent Beryllium Copper-tin System.*—Comparison of the diagram of Fig. 13 with that of Fig. 3 shows that with increasing beryllium content the entire diagram has been shifted in the direction of lower tin content and that a new phase, associated with the copper-beryllium system, has appeared and persists over a considerable portion of the diagram. A lowering of the liquidus and solidus temperatures can also be noticed.

The rapid decrease in the solubility of the alpha phase below 596° C. was found to be associated with the precipitation of a new phase designated as theta. This phase separates from the alpha as very fine needles which, during the annealing treatment, tend to coalesce and diffuse to the grain boundaries, although very slowly. When very small, the needles appear black, but when larger or more rounded the theta phase is found actually to be either white or gray, depending upon the orientation of the particle. Fig. 14 shows the typical structure in the alpha + theta field at 1000 dia. Evidence will be presented later to show that the theta phase is the gamma phase of the copper-beryllium system.

The 10 per cent tin alloy undergoes several interesting transformations in cooling from the peritectic temperature. Between this temperature and about 650° C. it is composed of alpha and a small amount of beta, the amount of beta constantly decreasing with falling temperature. Between 650° and about 590° C., the alloy consists of alpha alone, but on further cooling precipitation of the theta phase results and continues until the solubility becomes independent of temperature at about 400° C. Below 510° C., however, the delta phase also separates from the alpha in the form of blue angular particles exactly as in the 0.25 per cent beryllium system, although in a smaller amount.

Only indirect evidence was obtained with regard to the existence of a beta to beta prime transformation in this quasibinary section. On cooling the alloys in the alpha + beta region below 596° C., the theta phase was found to appear abruptly and the amount of this phase did not increase noticeably on cooling from 596° C. to room temperature. Precipitation of additional theta in needle form from the alpha did, however, occur during this fall in temperature.

The temperature of the formation of theta from the beta phase was found to be constant across the alpha + beta field at 596° C. and to rise sharply across the beta field. The above-mentioned abrupt formation of theta in the beta and not in the alpha leads to the belief that it is in some way connected with a change in the beta phase. The change at 596° C. was easily determined by thermal means in the alpha + beta field, even though the amount of theta involved was small, while the disappearance of theta could not be observed by thermal analysis in the gamma and gamma + delta fields where the amount of theta involved in the transformation was the same. This fact can be explained by assuming that the heat effect of the formation of theta was strengthened by a heat effect in the beta phase itself, since the intensity of the thermal effect increased with increasing tin content in the alpha + beta field. An almost identical curve for the beta prime transformation in the binary copper-tin alloys was determined by Hamasumi and Nishigori.

Thermal analysis consistently failed to distinguish between the two transformations or to find evidence of a beta to beta prime transformation at any other temperature. Since phase-rule considerations preclude the possibility of the two changes being coincident, it was assumed that the two phenomena occurred so close together as to be indistinguishable by thermal means. It seems possible that the beta to beta prime transformation occurs first on cooling and this change causes the precipitation of theta. In the absence of any evidence as to the actual mechanism of this double change, it was indicated only as a single line in the diagram. Fig. 15 shows the structure in the alpha + beta prime + theta field. The small white areas with black boundaries are theta, the large light areas alpha, and the matrix beta prime.

Owing to the presence of the theta phase, both the beta prime and gamma eutectoids have become invariant, the former at 562° C. and the latter at 613° C. Alloys quenched from below the beta prime eutectoid point contained, besides the alpha + delta eutectoid areas and the excess constituent (alpha or delta), small rounded areas of theta, unchanged after their formation. Characteristic needles of theta were observed in alpha areas, if alpha was the excess constituent. The gamma phase decomposed as in the 0.25 per cent beryllium alloys with the appearance of small blue spots. The temperature of the formation of delta from



gamma was found to have risen further to about 690° C. at approximately 31.5 per cent tin.

*The 1.0 Per Cent Beryllium Copper-tin System.*—The addition of 1.0 per cent beryllium to the copper-tin alloys (Fig. 16) causes a further shift of the diagram toward the region of lower tin content over that

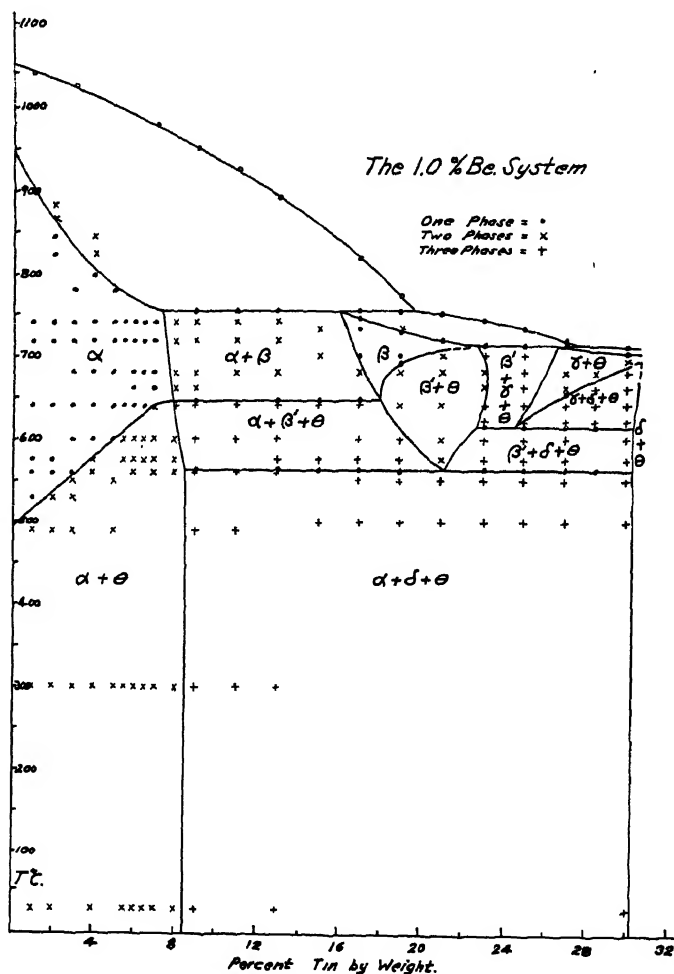


FIG. 16.—THE 1.0 PER CENT BERYLLIUM COPPER-TIN SYSTEM.

obtained with 0.5 per cent beryllium. In this quasibinary section, the alpha phase was not found to exist singly below 495° C. and the liquidus and solidus temperatures were found to be at still lower temperatures than in the 0.50 per cent beryllium diagram. The temperature at which the rounded form of the theta phase separated from the beta was found to be at a higher temperature (643° C.) than in the 0.50 per cent

beryllium alloys but the shape of the curve was the same. The amount of theta present in these alloys is considerably greater than that found in the 0.50 per cent beryllium alloys.

Fig. 17 shows the type of precipitation in the alpha + theta field. In order to be sure that the dark needles in this sample actually were the theta phase (white in color when completely resolved), a sample of the same composition was given the regular annealing treatment, cooled to room temperature, reheated to 600° C. for 7 days and quenched. The amount of coalescence can be seen by comparing Fig. 18 with Fig. 17, showing that the excess phase present actually was white. Even the smallest needles could be resolved at 1000 dia. as white or gray areas, as shown in Fig. 19.

Fig. 20 indicates the structures found in the alpha + beta prime + theta field, in which both types of theta precipitation were found, the needles being in the alpha and the large rounded areas in or at the edges of the beta prime phase. Both types of theta persisted on cooling to room temperature, although the beta prime phase broke down into the alpha + delta eutectoid.

In order to demonstrate that the needles and large rounded areas were one and the same phase, two samples were selected for powder-method X-ray analysis. One of these was a 6 per cent tin alloy (alpha + theta needles) and the other a 13 per cent tin alloy (alpha + delta + both types of theta), both samples being subjected to the regular annealing treatment and finally quenched from 300° C. A few lines not attributable to either alpha or delta were obtained from both samples, which, upon calculation, showed the theta phase to be body-centered cubic with a lattice parameter of about 2.69Å. This indicated that both types of precipitation were the same phase (theta). Furthermore, Dahl, Holm and Masing have stated that the gamma phase of the copper-beryllium system had an identical structure with a parameter of 2.70Å. This seems to show that the theta phase actually is the gamma phase of the copper-beryllium system. For this reason the alpha-phase boundary was extended below 1 per cent tin, the lowest tin alloy studied, to meet the temperature axis at 495° C. This is the value given by Borchers for the alpha-phase boundary of the copper-beryllium system at 1 per cent Be. The fact that the curve of the alpha-phase boundary in this 1.0 per cent beryllium quasibinary section is a straight line lends confirmation to the above interpretation.

The boundary marking the precipitation of theta from the beta phase was found to occur at a constant temperature of 643° C. in the alpha + beta field, to rise rapidly across the beta field and to pass either just below or just above the line denoting the peritectic reaction involving the formation of gamma. The temperature of this precipitation occurred so close to the peritectic transformation that it could not be distinguished



FIGS. 17-22.—CAPTIONS ON OPPOSITE PAGE.

from the latter by thermal means. All solid alloys investigated containing more than 22.9 per cent tin contained theta at all temperatures.

The beta to beta prime transformation was assumed to follow the upper boundary of the theta phase, since no evidence could be obtained of such a transformation at any other temperature. The double transformation was drawn as a single line, as in the 0.50 per cent beryllium diagram. The fact that the theta phase does not precipitate at the same temperature in this as in the 0.50 per cent quasibinary section in the alpha + beta region precludes the possibility of the two transformations being coincident.

Both the beta prime and gamma eutectoids were found to occur at the same temperature in this as in the 0.50 per cent Be section diagram, since the presence of theta rendered these transformations invariant. The structure present above and below the gamma eutectoid and in the immediate neighborhood of it can be seen in Figs. 21 and 22. The former is in the gamma + delta + theta area while the latter is of a sample of the same composition but quenched from below the gamma eutectoid transformation. It was extremely difficult to bring out the difference between theta (white) and delta (blue) in the photomicrograph of Fig. 22. The theta spots are slightly lighter in color than delta in the photomicrograph and are surrounded by heavy dark boundaries. The increase in the amount of delta and the change in its form brought about by the eutectoid can be seen by comparing these two photomicrographs.

Calculation of the X-ray diagram of the 13 per cent tin alloy quenched from 300° C., cited above, showed that the delta phase contained in it had the same complex face-centered cubic structure ascribed to it by Westgren and Phragmén in their work on the copper-tin system. The parameter was found to have decreased from 17.91Å. to 16.53Å. by the addition of the 1 per cent of beryllium. This shrinkage undoubtedly is due to solution of beryllium in the delta phase.

*The Ternary System.*—The isotherms of the ternary system were plotted from the results of the present investigation of the three quasibinary sections previously described, from the results of Borchers' work on the copper-beryllium system and from Carson's work on the copper-tin system. Stockdale's alpha-phase boundary of the copper-tin system

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FIG. 17.—7 PER CENT SN, 1 PER CENT BE. QUENCHED AT 700° C. ALPHA + THETA  
× 250.

FIG. 18.—7 PER CENT SN, 1 PER CENT BE. REHEATED 7 DAYS AT 600° C. AND  
QUENCHED. ALPHA + THETA. × 250.

FIG. 19.—7 PER CENT SN, 1 PER CENT BE. SAME TREATMENT AS FIG. 18. ALPHA +  
THETA. × 1000.

FIG. 20.—13 PER CENT SN, 1 PER CENT BE. QUENCHED AT 575° C. ALPHA (LIGHT) +  
BETA PRIME + THETA (WHITE SPOTS AND NEEDLES). × 250.

FIG. 21.—25 PER CENT SN, 1 PER CENT BE. QUENCHED AT 620° C. GAMMA (SPOTTED)  
+ DELTA + THETA (ROUNDED WHITE SPOTS). × 250.

FIG. 22.—25 PER CENT SN, 1 PER CENT BE. QUENCHED AT 575° C. BETA PRIME +  
DELTA (LIGHT) + THETA (WHITE WITH BLACK BOUNDARIES). × 250.

was used. The isotherms were drawn on an atomic per cent basis because of the small range of beryllium content investigated, the low atomic weight of beryllium serving to enlarge the scale on that side of the diagram. The calculated atomic percentages of the ternary alloys are given in Table 1.

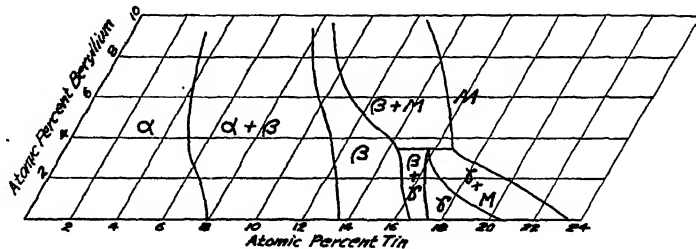


FIG. 23.—THE 730° C. ISOTHERM.

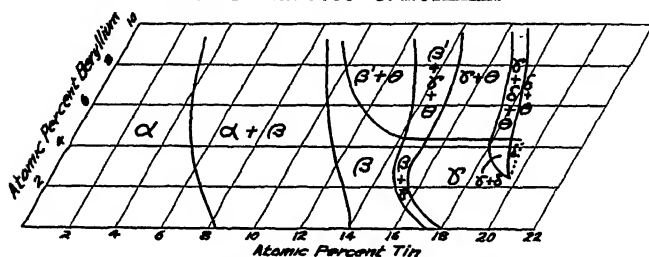


FIG. 24.—THE 680° C. ISOTHERM.

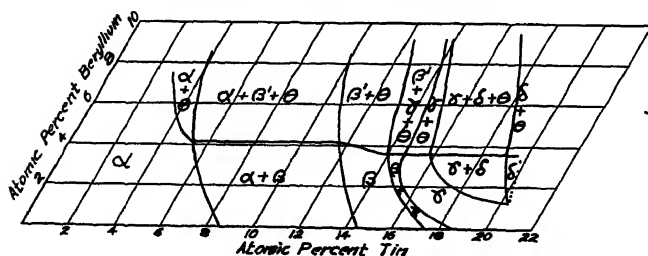


FIG. 25.—THE 630° C. ISOTHERM.

The course of the boundaries of the alpha and other copper-tin phases with increasing beryllium content could be followed easily. Because the quasibinary sections were taken parallel to the copper-tin system, the boundary of the theta phase could not be located within close limits, except when it crossed the quasibinary sections. At other points, general considerations of microstructure and the phase rule served to locate it closely enough for most purposes. Phase boundaries are indicated by full lines, while dotted lines show the behavior of the eutectoid points and the boundaries of the eutectoid areas where they do not correspond to phase areas.

The 730° isotherm (Fig. 23) indicates the solidification mechanism of the ternary alloys. Fig. 24, the 680° isotherm, presents the relations

existing in the solid alloys but above the formation temperature of either of the eutectoids. The theta phase is present at high tin and beryllium contents and the formation of delta from gamma can also be seen in the isotherm. The high-tin boundary of the delta phase was not determined, although a solubility was indicated. The appearance of the theta phase reverses the curvature of the boundary lines at higher beryllium contents.

At 630° (Fig. 25) alloys containing more than about 4 atomic per cent of beryllium contain theta. The point of crystallization of delta from

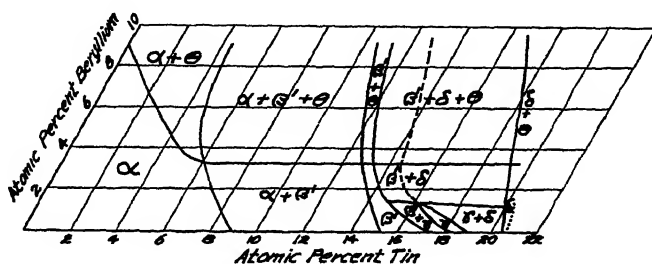


FIG. 26.—THE 575° C. ISOTHERM.

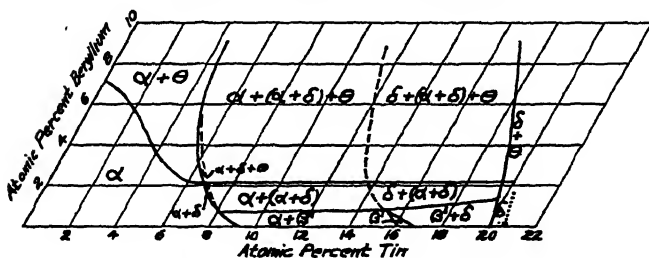


FIG. 27.—THE 530° C. ISOTHERM.

gamma has shifted to a lower beryllium content with fall in temperature. Fig. 26, the 575° isotherm, is above the gamma eutectoid of the copper-tin system and the mechanism of this transformation can therefore be seen in the figure. This eutectoid is drawn as a straight line sloping toward the copper-tin binary system at higher tin contents because the inversion was found to rise in temperature with increasing tin content in the 0.25 per cent beryllium quasibinary section, this fact indicating that less beryllium content was necessary at high than at low tin contents to enable the transformation to assume a constant temperature. In the absence of evidence to the contrary, the boundary of the theta phase was drawn as parallel to the copper-tin binary system, since the amount of theta in the alloys seemed to be substantially independent of tin content in this region. The dotted line in the beta prime + beta + theta field indicates the course of the gamma eutectoid point. The boundary of the theta phase was extended to meet the copper-beryllium binary

system in this and lower temperature isotherms at the point of appearance of the gamma phase of this system.

Fig. 27, the 530° isotherm, shows the mechanism of the alpha + delta eutectoid. The eutectoid line is shown as curving to higher beryllium content at the high-tin end because, in the 0.25 per cent beryllium quasibinary section, the eutectoid temperature decreased with increasing tin content. The rapid decrease in the size of the alpha-phase region with fall in temperature can also be observed. The dotted line indicates the course of the alpha + delta eutectoid point in the ternary system.

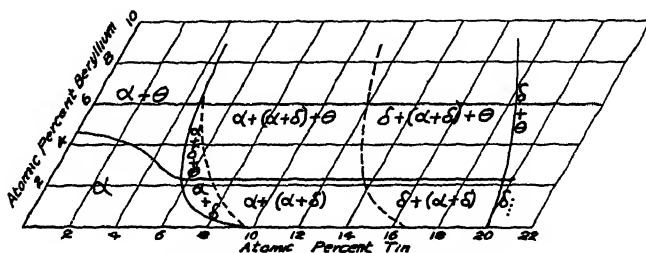


FIG. 28.—THE 300° C. ISOTHERM.

The 300° C. isotherm (Fig. 28) is substantially the same as that at room temperature. The effect of increasing beryllium content on the boundaries of the copper-tin phases can be readily seen. The small areas marked alpha + delta and alpha + delta + theta indicate that the delta phase present has separated from the alpha on cooling and that alloys in these areas do not contain the alpha + delta eutectoid. By comparing this diagram with Fig. 24, the extent of the precipitation-hardening range in the ternary system can be seen to be quite large.

### SUMMARY AND CONCLUSIONS

The ternary alloys of copper, tin and beryllium containing up to 32 per cent tin and 1.0 per cent beryllium were investigated by means of thermal analysis, X-ray determinations and quenching experiments, followed by microscopic examination of the quenched alloys. The results of the investigation are as follows:

1. The liquidus and solidus temperatures of the alloys were determined by means of thermal analysis and quenching experiments and were found to decrease uniformly with increase in beryllium content. The temperature of the peritectic reaction producing beta decreased from the value of 800° C. given by several investigators for the binary copper-tin alloys to 754° C. in the 1.0 per cent Be quasibinary section. Likewise, the temperature of the formation of gamma by its peritectic reaction was found to decrease from the value of 750° C., given by Carson for the copper-tin system, to 709° C. in the 1 per cent Be system.

2. All of the boundaries of the various phases were found to shift toward lower tin content with increase in beryllium content. The alpha field of the ternary system was found to decrease in size with decrease in temperature between about 650° C. and room temperature. This decrease undoubtedly accounts for the ability of certain of the alloys to respond to a precipitation-hardening treatment, an effect that was demonstrated by Masing and Dahl.

3. A new phase, designated as theta, was found to precipitate from the alpha in needle form and from the beta in the form of rounded spots at certain temperatures in the 0.5 and 1.0 per cent Be quasibinary sections. The amount of this phase present in the alloys increases with increase in beryllium content, but appears to be substantially independent of tin content. This phase is believed to be the gamma phase of the copper-beryllium system for the following reasons: (1) The theta phase could not be distinguished microscopically from the gamma phase in a copper-beryllium alloy subjected to the same thermal treatment; (2) X-ray determinations on two alloys containing theta showed that its structure and lattice parameter corresponded to the values given by Dahl, Holm and Masing for the gamma phase of the copper-beryllium system; (3) the boundary of the theta phase was found to intersect the 0 per cent tin intercept of the 1.0 per cent Be quasibinary section at a temperature that corresponded favorably with the value given by Borchers for the boundary of the gamma phase of the copper-beryllium system.

4. Thermal evidence was obtained of a transformation between 589° and 593° C. in the alpha + beta field of the 0.25 per cent Be quasibinary section. This transformation was accompanied by no observable microscopic change under equilibrium conditions, although short-time anneals in the transformation range disclosed a reaction rim, indicating a possible metastable state or intermediate phase. The change, therefore, was designated as of the beta to beta prime type. In the 0.5 and 1.0 per cent systems, the beta prime transformation was seemingly masked by the formation of the theta phase. The following reasons were advanced for the belief that the beta to beta prime transformation and the formation of the theta phase occurred very close together in the 0.5 and 1.0 per cent Be systems—so close, in fact, that thermal analysis consistently failed to distinguish between them: (1) No thermal evidence could be obtained of the beta to beta prime transformation at any other temperature; (2) the abrupt appearance of theta in the beta (or beta prime) constituent only at the transformation point indicated by thermal analysis and the persistence of the rounded theta spots without noticeable growth with further decrease in temperature, points to some change in the beta phase; (3) the disappearance of theta could be ascertained by thermal analysis in the alpha + beta and beta fields of the 0.5 and 1.0 per cent Be systems but not in the gamma or gamma + delta fields of



the 0.5 per cent system, which points to an additional thermal effect in the  $\alpha + \beta$  and  $\beta$  fields; (4) the shape of the transformation boundary in the 0.5 and 1.0 per cent systems was found to be almost identical with the course of the  $\beta$  to  $\beta'$  transformation in the binary copper-tin alloys as drawn by Hamasumi and Nishigori; (5) the two changes could not be coincident, since they do not occur at the same temperature with increasing beryllium content; they must be separated by some small temperature interval and it seems possible that the  $\beta$  to  $\beta'$  transformation occurs first on cooling and is immediately followed by the formation of  $\theta$ .

5. In the ternary alloys, the phase that breaks down into the  $\alpha + \delta$  eutectoid was shown to be  $\beta'$  and not  $\gamma$ . The  $\gamma$  phase could be readily distinguished from the  $\beta$  and  $\beta'$  phases by its darker color and characteristic decomposition on quenching. The  $\gamma$  phase was found to exist only at considerably higher temperatures than the eutectoid inversion and only at tin contents greater than that of the eutectoid point. The temperature of this inversion was found to increase with increase in beryllium content from the value of 520° C. usually given for it in the copper-tin system to 562° C. and remain constant with continued increase in beryllium content, since the presence of  $\theta$  makes the transformation invariant.

6. Evidence obtained on the ternary alloys indicated that  $\gamma$  underwent a eutectoid inversion into  $\beta'$  and  $\delta$ . The presence of a  $\gamma + \delta$  field (with or without  $\theta$ ) above the transformation temperatures, as indicated by thermal analysis, seems to preclude the possibility of the  $\delta$  phase being the result of a peritectoid reaction. Also, the intensity of the thermal arrest was found to decrease as the  $\delta$  side of the transformation was approached, which points to a eutectoid and not a peritectoid transformation. Furthermore, all microscopic evidence obtained from the  $\beta' + \delta$  field pointed to a transformation of eutectoidal character. The temperature of this inversion of  $\gamma$  increased with increasing beryllium content from 540° C. (Carson's value for the copper-tin system) to 613° C., and remained constant with further increase in beryllium content due to the presence of the  $\theta$  phase.

7. While the extent of the solubility of the  $\delta$  phase was not completely investigated, microscopic evidence definitely pointed to a range of solubility, which increased somewhat with increasing beryllium content. The temperature of the formation of  $\delta$  from  $\gamma$  rose with increase in beryllium content. The lattice structure of the  $\delta$  phase at its low-tin boundary was found to be of the complex type assigned to the  $\delta$  phase of the copper-tin system by Westgren and Phragmén. The lattice constant decreased at 1.0 per cent Be to 16.53Å. This sharp

decrease from 17.91 Å. (0 per cent Be) undoubtedly is due to beryllium in solution in the delta phase.

### ACKNOWLEDGMENTS

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### DISCUSSION

(W. P. Sykes presiding)

E. FETZ, \* New York, N. Y. (written discussion).—How do the investigators know that they attained the thermodynamic state of equilibrium? In particular, a certain section of the authors' constitutional diagram, according to our present knowledge, demands a revision; i.e., the low-temperature region in the vicinity of the copper-tin side (Fig. 28). Contrary to previous investigations, one of which, incidentally, is the paper of Eash and Upthegrove to which special reference is made in the present paper, the solubility of tin in copper drops materially with falling temperatures. The Russian investigators Konobejewski and Tarassowa recently found, by means of X-rays, that the solubility of tin in copper is 8.5 atomic per cent at 480° C. and only 4 atomic per cent at 300° C. Their calculations, based on the Thompson-Freundlich equation, covering the equilibrium between minute crystals and the solid, under-cooled solution

$$RT \ln \frac{S}{S_{\infty}} = \frac{2\sigma M}{\rho l} \quad [1]$$

\* Special Student, X-Ray Department, School of Mines, Columbia University.

leads to a saturation concentration at 300° C. of only  $S_{\infty}^{300} = 2.22$  atomic per cent Sn and integration of van't Hoff's equation for solutions

$$\ln S_{\infty} = \frac{Q}{RT} + b \quad [2]$$

furnishes a "true solubility" of  $S_{\infty}^{300} = 2.5$  atomic per cent Sn instead of 4.0 atomic per cent Sn as found experimentally. It thus appears that the entire low-temperature range of the authors' Cu-Be-Sn equilibrium is not in a thermodynamic state of equilibrium at the Cu-Sn side.

Those who have quantitatively studied the low diffusion speed during the breakdown of (mildly supersaturated) solid solutions at relatively low temperatures realize the great difficulties in establishing an equilibrium diagram in this temperature range. The difficulties mainly arise from two sources: (1) the experimental technique of discovering the heterogeneity of slightly supersaturated solid solutions at low temperatures and (2) the peculiar behavior of certain undercooled supersaturated solutions to remain in that metastable state more or less indefinitely.

The thermal analysis is naturally quite useless at these relatively low temperatures where the breaking down of the homogeneous alpha phase is suppressed, delayed or extended over hundreds of hours. The microscope has a limited range of identifying the precipitating or precipitated phase in alloys close to the alpha-phase boundary line. At elevated temperatures, the mobility in the space lattice is comparatively large and the thermodynamic state of equilibrium is attained after relatively short times. In view of the exponential functions correlating diffusion speed to temperature, there is no reason to assume that the annealing time of 1 hour at 750° C. as applied by Masing and Dahl in their experiments on Cu-Sn-Be alloys is "undoubtedly too short," but it appears very doubtful that "over 500 hr." represents a sufficiently long anneal for alloys around 300° C. At higher temperatures, microscopic examination provides for reliable results. At relatively low temperatures, the establishing of equilibrium conditions takes considerably longer times, especially with alloys close to the alpha boundary line. The diffusion speed is reduced to such an extent that equilibrium is not reached in a reasonable time.

A further reason why microscopic examination fails at very low temperatures is that when the temperature is lowered the number of nuclei increases whereas the crystallization speed greatly decreases, so that the heterogeneity of an alloy cannot be detected at the highest magnifications. If the number of nuclei is large, that is, in highly disperse precipitation, the parent solid solution is still supersaturated after its breakdown. The degree of supersaturation can be evaluated by means of equation 1. Many metallurgical investigations indicate the submicroscopic decomposition of a homogeneous solid solution by determinations of abrupt changes of physical properties, notably of electrical conductivity and hardness.

X-ray analysis, as a matter of fact, offers distinctive advantages, since the saturation of the alpha phase at any temperature need not be determined on a sample close to the alpha-phase boundary. An alloy of the greatest amount of supersaturation and even one of the two-phase region can be utilized. Owing to the greater amount of supersaturation and to the (usually) lower melting point (and, therefore, probably larger diffusion speeds) the breakdown of the homogeneous alpha phase readily takes place and the end of this process can be conveniently established by the sharpness of the interference lines of the largest deviation angles, assuming that a reasonable lattice-constant change occurs. Thus the alpha-phase boundary line can be determined directly, accurately and efficiently by using one sample for each temperature instead of narrowing down the boundary line by determining the heterogeneity of several alloy samples in the vicinity of the unknown boundary line by means of the microscope.

The next source of error is attributable to the tendency of some undercooled solid solutions, as, for instance, copper-tin alloys, to remain in this state indefinitely. Several years ago, Tammann pointed out that there is a certain minimum temperature at which the thermodynamic state of equilibrium cannot be established because of the low mobility of the atoms. However, the mobility in the space lattice at lower temperatures and thus the breakdown of solid solutions, the formation of crystal nuclei and subsequent crystal growth can be accelerated considerably without increase of temperature or concentration by putting the alloy into a state of higher internal energy by cold-work. The theory of nucleus formation in undercooled solutions has been advanced recently by Joost and his coworkers, who started from the fundamental concepts held by Gibbs and who recognized the paramount significance of the surface energy of minute crystals in the surrounding solution.

It is surprising that physical metallurgists make so little use of combined mechanical and thermal treatments with the object of establishing thermodynamic equilibrium conditions. The possibilities of this procedure are clearly shown in the Cu-Sn system. As to the divergencies between the theoretical solubility at, say, 300° evaluated on thermodynamic grounds and the experimental X-ray determination, it is evident that the latter value must depend on the amount of cold-work administered as well as on temperature and supersaturation. It would be interesting to determine how closely the theoretical and experimental values can be brought into agreement by applying alternately severe cold-working and annealing. When this is accomplished, the final course of the alpha-phase boundary line in the authors' Fig. 28 can be drawn up, while at present it can only be qualitatively said that the suggested shape is incorrect.

It would not be difficult to determine whether, in accordance with the present constitutional diagram, samples of heat No. 1 with 1.82 atomic per cent Be, 5.53 atomic per cent Sn and 92.65 atomic per cent Cu actually remain homogeneous at low temperatures. Since no equilibrium conditions are prerequisite to establishing the heterogeneity by hardness measurements or by determinations of electrical conductivity, it would be advisable to trace the hardness or conductivity in moderately cold-worked specimens of heat No. 1 at temperatures below 300°.

There is hardly a more striking example of the significance of the alpha-phase boundary line than beryllium-bearing alloys rich in copper. Owing to the powerful hardening ability of beryllium, beryllium bronzes have been developed, which are unsurpassed by any nonferrous alloy in increase of strength by precipitation-hardening. In the second place, the prohibitive price of beryllium calls for an economic use of this element whereby the knowledge of the proper shape of the alpha space would be of great practical value. Regarding the economic use of beryllium, it must be regretted that the authors did not succeed in establishing the stoichiometric composition of the precipitating phase. Several times, crystal-structure determination by X-rays has been applied with success for identification of the precipitant in alloys subject to age-hardening. It will be interesting to compare the forthcoming X-ray investigations of Mikulas and Thomassen with the present work. It is highly probable that in the higher tin regions, where the present authors were not handicapped by difficulties in the nature of the experimental technique, the forthcoming X-ray work will substantially corroborate the authors' extensive, skillful and elaborate research work.

# Free Energy and Heat of Formation of the Intermetallic Compound CdSb

BY HARRY SELTZ\* AND J. C. DEHAVEN\*

(New York Meeting, February, 1935)

INTERMETALLIC compounds are formed in many binary metal systems. Some compounds are stable to their melting points, and others decompose at lower transition temperatures. Even those of the first class are dissociated in the liquid state, as indicated by the continuous form of their solubility curves at their melting points<sup>1</sup>. While the lattice structures of some of these compounds have been determined, their thermodynamic properties have not been investigated. In this paper is described the determination of the free energy and heat of formation of the compound CdSb, which is of the first class mentioned above, melting congruently at 455° C. This compound shows a rhombic structure, and the lengths of the edges of the elementary cell containing four molecules are:  $a = 6.52$ ,  $b = 8.60$ ,  $c = 4.16 \text{ \AA}$ .<sup>2</sup>

There are three possible methods of determining the free energy of formation of a compound of this type. The first method, applying the third law of thermodynamics, requires the measurement of its heat capacity preferably to liquid hydrogen temperatures, and a calorimetric determination of its heat of formation. The second method involves the study of the equilibrium of the compound in some gas reaction, such as:



From the known free energies of formation of CdO, CO<sub>2</sub> and CO the free energy of formation of CdSb could be calculated. The third method measures the electromotive force of a galvanic cell in which the cell reaction is the reversible formation of the compound from the elements. The first method is generally applicable, but requires elaborate experimental equipment. The second method can not be used for compounds melting at low temperatures, owing to the difficulty in establishing equilibrium. The electromotive force method, therefore, seemed to offer

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\* Department of Chemistry, Carnegie Institute of Technology, Pittsburgh, Pa.

<sup>1</sup> Lewis and Randall: *Thermodynamics*, 217. New York, N. Y. McGraw-Hill Book Co.

<sup>2</sup> F. Halla and J. Adler: *Ztsch. anorg. allgem. Chem.* (1929) 185, 184.

most promise for this investigation, and preliminary study indicated that a satisfactory reversible cell could be designed for temperatures up to 450° C. using a molten salt electrolyte. Furthermore, from measurements of the change of electromotive force of the cell with change of temperature, the heat of formation of the compound can be calculated by well-known thermodynamic methods.

### *Experimental Procedure*

The part of the phase diagram<sup>2</sup> for the cadmium-antimony system that is of interest in this investigation is reproduced in Fig. 1. The compound CdSb melts at 455° C., and a eutectic between Sb and CdSb forms at 445° C. (40 per cent Cd). A second compound Cd<sub>3</sub>Sb<sub>2</sub> also exists and the dotted lines represent the metastable formation of this compound. This region can be achieved by undisturbed cooling under a carnallite melt<sup>3</sup>. With agitation or seeding, however, only the stable CdSb is formed. The method of preparing the CdSb electrodes, described below, prevented the formation of the metastable form, as shown by the fact that they exhibited no melting until the stable eutectic temperature of 445° C. was reached.

The electromotive force measurements in this investigation were made in Pyrex H-cells, constructed from 0.8-cm. tubing. The vertical legs were about 30 cm. long and were held 2 cm. apart by the connecting cross tube, which was about 2 cm. above the closed ends. Near the tops of the vertical tubes side arms were sealed in leading through a Y to a Hyvac pump. The electrolyte used was a eutectic mixture of lithium and potassium chlorides (56 per cent KCl) melting at 352° C., to which was added about 6 per cent of cadmium chloride. This electrolyte was fused and cast into sticks, which were kept in a drying oven until used. Sufficient of this electrolyte was introduced into the H-cell to fill the cross tube completely when melted. In one leg of the cell was placed 1 gram of pure cadmium, which melted under the fused electrolyte to form a bright surfaced electrode which showed no oxidation at the completion of any of the runs. Electrical connection was made to this electrode by a tungsten wire lead (0.25-mm. diameter) which was sealed into a Pyrex tube so that the wire barely projected through the seal. This lead tube extended out of the cell through a cork stopper which was made vacuum-tight with shellac. Connection from the tungsten wire to the potentiometer was made by welding to a copper lead.

To insure the absence of thermal or other parasitic electromotive forces, cadmium electrodes were first placed in both legs of the cell, with the projecting tungsten leads completely immersed in the molten metal.

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<sup>2</sup> Kurnakov and Konstantinov: *Zitsch. anorg. Chem.* (1908) 58, 1.

The cell was heated in a vertical chromel-wound furnace and evacuated to a pressure of 0.01 mm. by the Hyvac pump. When all gas bubbles were removed from the electrolyte and from the surface of the electrodes the electromotive force of this cell showed a maximum value of  $\pm 0.05$  mv. in the temperature range of 380° to 450° C. After being in contact with the molten cadmium for a period of two days, the tungsten leads showed no apparent deterioration.

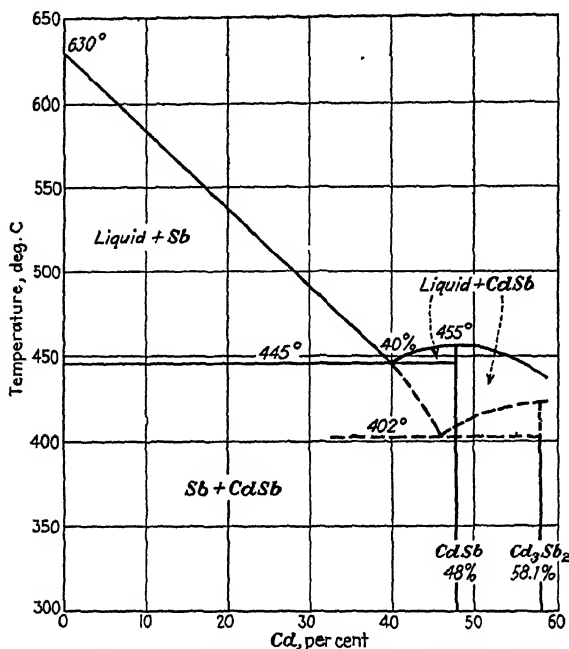
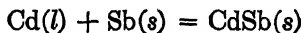
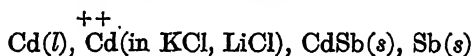


FIG. 1.—PHASE DIAGRAM FOR CADMIUM-ANTIMONY SYSTEM, TO 60 PER CENT Cd.

*Preparation of CdSb Electrodes.*—The cell reaction of which the electromotive is to be measured is:



which requires for its reversible operation a cell set-up as follows:



The CdSb electrode should therefore consist of a mixture of the solid compound and solid antimony. From the phase diagram of the system, Fig. 1, it can be seen that any melt containing less than 48 per cent Cd will solidify stably with these solid phases present. Electrodes of three different compositions, 40, 43 and 37 per cent Cd, were used in this investigation. These correspond to compositions at and on each side

of the eutectic. They were prepared by melting weighed amounts of the two pure components in a small crucible under the fused electrolyte, which entirely prevented oxidation. The small molten globule (0.5 gram) was stirred with a tungsten-lead while cooling to prevent the formation of  $\text{Cd}_3\text{Sb}_2$ . As the alloy began to solidify the tungsten tip was forced down into it and solidification took place under the fused salt. When cool this electrode adhered tightly to the tungsten tip and covered it completely. It had a dark metallic luster and the presence of the stable  $\text{CdSb}$  was established by the fact that these electrodes remained solid up to the eutectic temperature of  $445^\circ \text{C}$ .

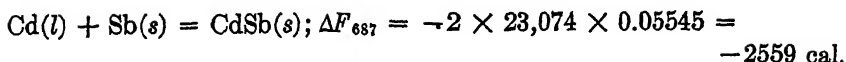
The complete cell was set up as indicated above. Under the molten electrolyte in one leg of the H-cell was placed the cadmium electrode with the immersed tungsten lead, and the  $\text{CdSb}$  electrode was placed in the other leg. The cell was made gas-tight by shellacking the cork stoppers through which the lead tubes passed. The cell was placed in the furnace, evacuated to a pressure less than 0.01 mm. and the electromotive force was measured on a Leeds & Northrup type K potentiometer. The temperature was measured by an iron-chromel thermocouple calibrated at the melting points of tin, lead and zinc.

### *Measurements and Calculations*

After complete removal of gas bubbles from the electrolyte and from the surfaces of the electrodes by evacuation, the cells appeared to come to equilibrium quickly, and steady, reproducible e.m.f. readings were obtained. The temperature of the well insulated furnace was satisfactorily controlled by hand, since practically simultaneous e.m.f. and temperature readings could be taken. Two electrodes of each composition were used and readings were taken at temperature intervals between  $440^\circ$  and  $395^\circ \text{C}$ ., both cooling and heating. For a given composition the results were reproducible within  $\pm 0.1$  mv. These results are tabulated for the three compositions in Table 1. In Fig. 2 the e.m.f. values are plotted against the temperatures and it is apparent that they fall on a straight line with maximum deviation of  $\pm 0.2$  mv. for the different compositions. This is direct indication of the reversible nature of the cell reaction. As a further test the concentration of  $\text{CdCl}_2$  in the electrolyte was varied without producing any change in the e.m.f. of the cells.

The free energy change  $\Delta F$  of a cell reaction is related to the reversible electromotive force  $E$  of the cell by the equation,  $\Delta F = -NEF$ , where  $N$  is the number of equivalents involved and  $F$  is the Faraday equivalent (23,074 cal. per volt equivalent). Taking the mid-temperature of the measurements as a reference point we find  $E = 0.0545$  volt at  $414^\circ \text{C}$ ., and for the reaction,





To express  $\Delta F$  as a function of the temperature the heat of the reaction must be known. Since the slope of the e.m.f.-temperature curve is

TABLE 1.—*Temperature Readings*

37 Per Cent Cd		40 Per Cent Cd		43 Per Cent Cd	
Temp., Deg. C.	<i>E</i> (volts)	Temp., Deg. C.	<i>E</i> (volts)	Temp., Deg. C.	<i>E</i> (volts)
394.5	0.05683	393.0	0.05682	395.8	0.05675
396.3	0.05670	395.0	0.05668	397.0	0.05653
397.5	0.05660	398.0	0.05650	398.6	0.05644
400.0	0.05649	401.0	0.05634	401.0	0.05640
402.0	0.05641	403.1	0.05612	403.0	0.05621
404.0	0.05629	404.6	0.05601	404.8	0.05614
406.5	0.05606	406.0	0.05590	406.5	0.05601
408.0	0.05599	409.0	0.05580	408.8	0.05584
411.0	0.05562	411.3	0.05574	410.7	0.05572
413.5	0.05550	414.5	0.05541	412.0	0.05555
416.0	0.05531	416.0	0.05526	414.0	0.05541
418.0	0.05515	418.1	0.05510	416.6	0.05537
420.5	0.05508	420.0	0.05499	418.2	0.05517
422.3	0.05500	422.5	0.05482	420.5	0.05497
424.0	0.05480	424.0	0.05466	422.2	0.05487
427.0	0.05470	427.0	0.05450	425.2	0.05470
430.0	0.05436	429.0	0.05438	427.3	0.05446
434.5	0.05400	432.6	0.05420	430.2	0.05430
		434.5	0.05400	434.5	0.05398
				436.0	0.05390

constant over the range investigated, the Gibbs-Helmholtz equation can be employed to calculate this quantity. This equation is,  $T \left( \frac{dE}{dT} \right) = E + \frac{\Delta H}{NF}$ , where  $T$  is the absolute temperature  $\left( \frac{dE}{dT} \right)$  is the slope of the e.m.f.-temperature curve and  $\Delta H$  is the heat of reaction (heat-content change). From Fig. 2,  $\left( \frac{dE}{dT} \right) = -0.0000685$  volt per deg. C., and  $\Delta H = 46,148 [-687 \times 0.0000685 - 0.05545] = -4730$  cal. Furthermore, this  $\Delta H$  value would change very slightly with the temperature, since the change in heat capacity,  $\Delta C_p$ , for the reaction would be small.  $\Delta F$  can then be expressed as a function of the temperature by the equation,  $\Delta F = \Delta H + IT$ , where  $I$  is a constant of which the value can be calculated from the value of  $\Delta F$  at  $414^\circ$  C. ( $687^\circ$  abs.).

$$I = \frac{-2559 + 4730}{687} = 3.160 \text{ cal. deg.}^{-1}$$

Hence,  $\Delta F_T = -4730 + 3.160T$ , and at the melting point of Cd,  $\Delta F_{594} = -2852$  cal. and we can write for the reaction  $\text{Cd}(s) + \text{Sb}(s) = \text{CdSb}(s)$ ,  $\Delta F_{594} = -2852$  cal.  $\Delta H$  for this reaction is obtained by adding

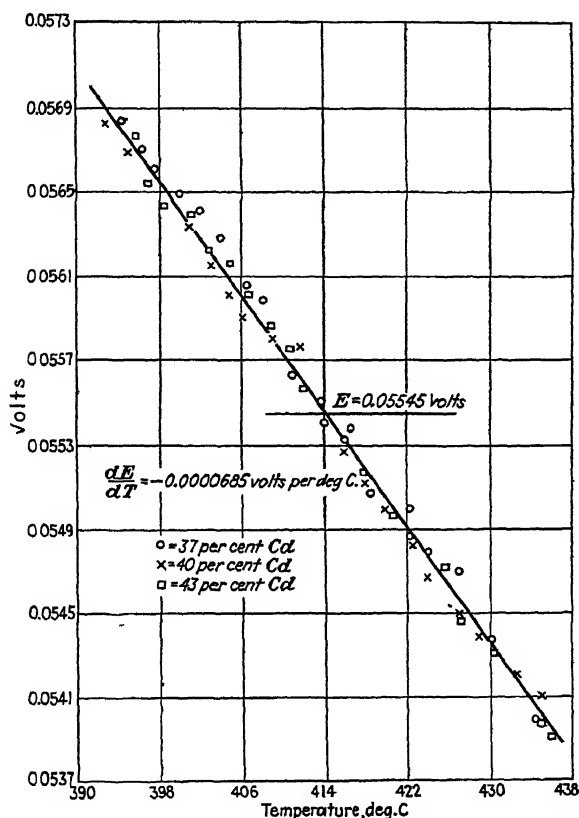


FIG. 2.—ELECTROMOTIVE FORCE PLOTTED AGAINST TEMPERATURE.

the heat of fusion of Cd, 1244 cal., to the heat of the reaction involving liquid cadmium, giving a value of  $\Delta H$  of  $-3486$  cal. Again, expressing this reaction as a function of the temperature;

$$I = 1.067, \text{ and } \Delta F_T = -3486 + 1.067T$$

and  $\Delta F_{298} = -3168$  cal. From the equation  $\Delta F = H - T\Delta S$ , where  $\Delta S$  is the change in entropy, we calculate for this reaction  $\Delta S_{298} = -1.1$  cal. deg.<sup>-1</sup>, and taking the entropy per gram-atom for Sb as 10.5 and for Cd as 12.3 we calculate the entropy of CdSb,  $S_{298} = 21.7$  cal. deg.<sup>-1</sup>.

## SUMMARY

1. The thermodynamic properties of the intermetallic compound CdSb are determined by an electromotive force method.

2. For the reaction,  $\text{Cd}(s) + \text{Sb}(s) = \text{CdSb}(s)$ ,

$$\Delta F = -3486 + 1.067T, \text{ and } \Delta F_{298} = -3168 \text{ cal.}; \Delta H = -3486 \text{ cal.}$$

3. The entropy change in this reaction is small,

$$\Delta S_{298} = -1.1 \text{ cal. deg.}^{-1} \text{ and for CdSb, } S_{298} = 21.7 \text{ cal. deg.}^{-1}.$$

# Thermal and Electrical Conductivities of Copper Alloys

BY CYRIL STANLEY SMITH,\* MEMBER A.I.M.E. AND EARL W. PALMER,\* JUNIOR  
MEMBER A.I.M.E.

(Chicago Meeting, October, 1935)

FOR several years an investigation has been in progress in the research laboratory of The American Brass Co. to determine the thermal and electrical conductivities of most copper alloys of commercial importance and several of scientific interest. This paper contains such data on the binary alloys of copper with silicon, aluminum, manganese and nickel, and on a large number of ternary or more complex alloys. Some interesting general relationships between the thermal and electrical conductivities for all copper alloys at all temperatures are pointed out. The data for the copper-zinc, copper-phosphorus and copper-tin binary systems have already been published<sup>1,2</sup> † except for the electrical conductivity at 200° C., which is given in the appendix of this paper.

## LITERATURE ON THERMAL CONDUCTIVITY OF COPPER ALLOYS

The papers referred to above contained a summary of the figures available in 1929 for the thermal conductivity of copper alloys. There is given in Table 1 herewith a selection of the data that have appeared since that time. The measurements of Hanson and Rogers<sup>3</sup> are particularly interesting since they cover a series of alloys in the alpha solid solution range and show the effect of heat-treatment. Their alloys were tested as annealed castings, and are not therefore directly comparable to the worked alloys measured in the present investigation, although the difference is small. Bailey's determinations<sup>4</sup> were carried out on the alloys used by Lees<sup>5</sup> in 1906, and extend his results to higher temperatures. It is most unfortunate that the alloys were not analyzed, for the approximate compositions given are hardly sufficient identification of the material. It is equally to be regretted that neither Hanson and Rogers nor Bailey give data for the electrical conductivities of their samples. Sager<sup>6</sup>, using the heat-wave method of King, determined the thermal conductivity of copper, nickel and four alloys of the two metals. His results are included in Table 1.

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\* Copper Alloys Research Laboratory, The American Brass Co., Waterbury, Conn.

† References are at end of paper.

TABLE 1.—*Results of Other Investigations on Thermal Conductivity of Copper Alloys*

Investigator	Com- position, Per Cent	Ave. Temp., Deg. C.	Thermal Conduct. Cal. per Cm. per Sec. per Deg. C.	Com- position, Per Cent	Ave. Temp., Deg. C.	Thermal Conduct. Cal. per Cm. per Sec. per Deg. C.
Hanson and Rogers <sup>a</sup> .....	1.75 Al	165	0.405	0.78 Ni	165	0.655
	5.10	165	0.256	1.57	165	0.562
	8.45	165	0.219	2.76	165	0.425
	12.78	165	0.169	4.90	165	0.310
	0.083 P	165	0.708	0.070 As	165	0.695
	0.135	165	0.504	0.144	165	0.501
	0.229	165	0.398	0.302	165	0.398
	0.406	165	0.292	0.495	165	0.292
	0.20 Fe	165	0.702 <sup>a</sup>	0.20 Fe	165	0.713 <sup>a</sup>
	0.29	165	0.640 <sup>a</sup>	0.29	165	0.603 <sup>a</sup>
	0.50	165	0.505 <sup>a</sup>	0.50	165	0.580 <sup>a</sup>
	1.07	165	0.342 <sup>a</sup>	1.07	165	0.570 <sup>a</sup>
Bailey <sup>a</sup> .....	Brass	78	0.305	Platinoid	159	0.0871
	(approx. 70/30)	96	0.312	(approx. 15 Ni	216	0.0915
		120	0.323		305	0.108
		164	0.340	22 Zn	415	0.117
		208	0.342	63 Cu)		
		430	0.350			
Sager <sup>a</sup> .....	20 Ni	20	0.084	60 Ni	20	0.059
		200	0.100		200	0.074
20° C. results extrapolated	40 Ni	20	0.059	80 Ni	20	0.081
		200	0.075		200	0.092

<sup>a</sup> Quenched from 1000° C.<sup>b</sup> Quenched from 650° C.

## MEASUREMENTS IN PRESENT INVESTIGATION

*Thermal Conductivity.*—The apparatus used for the present investigation was essentially that described and illustrated in the first paper of this series, although some minor improvements were made. In the earlier experiments frequently bubbles of air collected in the cooling head and upset the rate of flow. This difficulty was obviated by heating the feed water with steam and allowing it to remain in an open tank for the elimination of air bubbles; it was then cooled and passed to the constant-level tank, in which a sensitive thermostatic control was fitted. In many runs, the differential couple previously used to measure the difference in temperature of incoming and outgoing water was replaced by two carefully calibrated thermometers.

The temperature gradient along the specimens (which were 0.75-in. diameter and 8 in. long over the measured section) was determined by three copper-constantan thermocouples. To facilitate changing the bars,

the couples were not pegged into place but were introduced through horizontal tubes through the guard ring, and held in holes drilled for them in the specimen by an elastic band around the outside of the apparatus. Couples in the guard ring assisted in the adjustment of its gradient to match that of the bar. When there was an appreciable difference of temperature between guard ring and bar, corrections for lateral heat flow were made, but these were always very small.

At least one series of measurements, giving values of the conductivity at three different mean temperatures, was made with the heater controlled at each of the temperatures 250° and 125° C., the cold end of the bar being held at about 25° C. Within the precision of the determination, the experimental points, covering the range 40° to 230° C., lay upon a straight line, from which values at 20° and 200° C. were read and the temperature coefficient calculated. For no apparent reason the lines through the two series of points obtained with different temperature gradients would often show a slight parallel displacement.

Thermal conductivity measurements, so simple in principle, are extraordinarily difficult to perform with high precision. The temperature gradient and the calorimetric water flow rate and difference in temperature are easily measured to one per cent, yet comparable precision in the final figure is exceptional.

*Electrical Conductivity.*—The electrical conductivity was determined on the identical specimens used for the thermal measurements. The potential drop across the bar was compared with that across a standard resistance, reversed readings being taken to avoid thermoelectric effects, which were very small. The bar was immersed in an oil bath controlled by hand for the 20° C. measurements,\* and automatically controlled within  $\pm 0.1^\circ$  C. at 200° C.

The electrical conductivity at 200° C. had not been measured at the time the earlier papers were published. The conductivity at this temperature of the bars therein reported is given in Appendix A, together with the temperature coefficient of resistance and the Lorenz ratio at 200° C.

*Preparation of Material.*—Many of the specimens measured were commercial alloys, taken from stock or prepared in the mills of The American Brass Co. in the customary fashion. Alloys not in normal production were melted and cast in the laboratory. All alloys were analyzed† for the principal constituent elements and impurities.

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\* The electrical conductivity measurements at 20° C. were made as routine determinations at the Ansonia testing laboratory of The American Brass Co., under the direction of Mr. C. F. Schmid or Mr. I. T. Hook, whose cooperation is gratefully acknowledged.

† For this painstaking analytical work the authors wish to thank members of the

## RESULTS

The results of the measurements on the binary alloys are given in Table 2 and Figs. 1 to 6, and the properties of the miscellaneous alloys are summarized in Table 3.

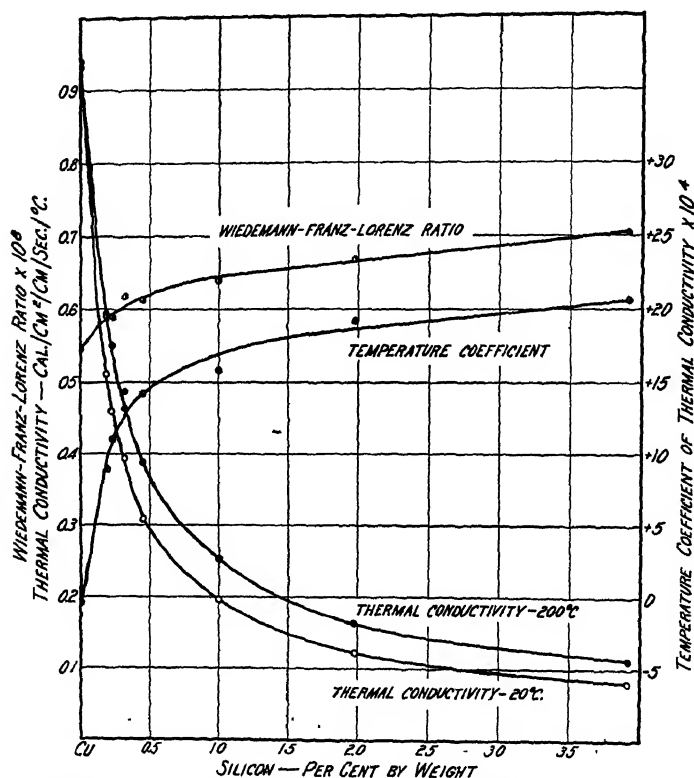


FIG. 1.—THERMAL CONDUCTIVITY OF COPPER-SILICON ALLOYS IN  $\alpha$  SOLID SOLUTION RANGE.

*Copper-silicon System.*—These alloys were hot-rolled from laboratory castings  $2\frac{1}{2}$  in. in diameter, cold-drawn to  $\frac{1}{8}$ -in. diameter and annealed at  $700^{\circ}\text{C}$ . All were homogeneous  $\alpha$  solid solutions and the conductivity decreases with increasing silicon content, as Fig. 1 shows. At the same time the temperature coefficient increases and the Lorenz ratio rises, at first rapidly and afterwards more slowly. Some industrially important ternary alloys containing silicon will be found in Table 3.

chemical laboratory of The American Brass Co., working under the direction of Mr. C. H. Davis.

TABLE 2.—*Electrical and Thermal Properties of Copper Alloys*

Bar No.	Composition, Per Cent by Weight				Heat-treatment		Elec. Cond. Per Cent I.A.C.S. at 20° C.	Elec. Cond., $\lambda$ Ohm <sup>-1</sup> per Cm. $\times 10^{-4}$		Temp. Coef. of Resist. (20°-200°) at 20° C.	Thermal Conductivity K, Cal. per Sq. Cm. per Cm. per Sec. per Deg. C.		Temp. Coef. of Thermal Cond. (20° C.) at 20° C.	Wiedemann-Franz-Lorenz Ratio $\frac{K}{\lambda T} \times 10^9$		Bar No.
	Other Elements				Deg. C.	Hours		20° C.	200° C.		20° C.	200° C.		293° K	473° K	
Copper-silicon Alloys																
2	0.00	99.986	0.0016	O, 0.022 S, 0.0015-	550	1	101.66	58.962	34.16	0.00392	0.941	0.934	-0.00004	5.45	5.78	2
104	0.19	99.80	0.02		700	2	50.99	29.58	21.30	0.00215	0.510	0.592	+0.00089	5.89	5.88	104
105	0.23	99.78	0.02		700	2	45.37	26.60	19.80	0.001905	0.459	0.550	0.00110	5.89	5.87	105
86	0.32	99.65	0.032	Pb, 0.00	700	1	37.44	21.71	16.98	0.001541	0.394	0.487	0.00131	6.19	6.06	86
106	0.45	99.53	0.03		700	2	29.64	17.19	13.96	0.001280	0.309	0.388	0.00142	6.14	5.87	106
78	1.00	99.06	0.03		700		18.11	10.50	9.13	0.000835	0.197	0.253	0.00158	6.40	5.86	78
79	1.98	98.09	0.05		700		10.75	6.235	5.659	0.000563	0.122	0.164	0.00191	6.68	6.13	79
80	3.91	96.00	0.02		700		6.802	3.945	3.655	0.000438	0.081	0.112	0.00206	7.04	6.47	80
Copper-aluminum Alloys																
99	0.07	99.95	0.01		750	2	90.66	52.58	31.69	0.00366	0.842	0.861	+0.00012	5.46	5.74	99
100	0.22	99.77	0.01		750	2	72.27	41.91	27.59	0.00287	0.696	0.744	0.00038	5.68	5.70	100
101	0.47	99.47	0.02		750	2	55.34	32.10	22.91	0.00223	0.561	0.623	0.00061	5.96	5.74	101
76	0.71	99.20	0.09		700		40.34	23.40	17.95	0.001683	0.418	0.498	0.00106	6.10	5.86	76
77	1.89	98.08	0.03		700		27.42	13.91	13.00	0.001241	0.293	0.369	0.00144	6.29	5.99	77
45	4.61	95.25	0.14		700	2	17.69	10.26	8.824	0.000906	0.198	0.256	0.00160	6.60	6.13	45
46	7.72	92.15	0.13		750	3½SC	15.23	8.834	7.650	0.000855	0.173	0.224	0.00154	6.69	6.19	46
102	9.37	90.56	0.07		750	2VSC	14.31	8.24	7.056	0.000934	0.156	0.200	0.00157	6.47	5.99	102
50	9.90	89.88	0.22		750	3½SC	13.66	7.923	6.724	0.000983	0.157	0.199	0.00149	6.76	6.25	50
130	12.15	87.76	0.09		750	2VSC	11.94	6.925	5.738	0.00115	0.128	0.161	0.00140	6.92	5.90	130



TABLE 2.—(Continued)

Bar No.	Composition, Per Cent by Weight				Heat-treatment		Elec. Cond. Per Cent I.A.C.S. at 20° C.	Elec. Cond., $\lambda$ Ohm <sup>-1</sup> per Cm. $\times 10^{-4}$		Temp. Coef. of Elect. Resist. (20°-200°) at 20° C.	Thermal Conductivity K, Cal. per Sq. Cm. per Sec. per Deg. C.		Temp. Coeff. of Thermal Cond. (20°-200°) at 20° C.	Wiedemann-Franz-Lorenz Ratio $\frac{K}{\lambda T} \times 10^8$		Bar No.	
					Deg. C.	Hours		20° C.	200° C.		20° C.	200° C.		293° K	473° K		
Copper-nickel Alloys																	
107	0.28	99.73	0.01			800	2	78.81	45.70	29.11	0.00315	0.769	0.775	+0.00004	5.74	5.62	107
108	0.54	99.47	0.02			800	2	68.86	39.94	26.86	0.00270	0.698	0.718	0.00016	5.96	5.65	108
109	1.97	97.94	0.02			800	4	39.15	22.71	17.58	0.001613	0.410	0.481	0.00096	6.16	5.78	109
110	5.09	94.92	0.01			800	4	21.37	12.39	10.64	0.00012	0.238	0.297	0.00138	6.56	5.90	110
111	10.07	89.90	0.02			800	4	12.19	7.07	6.460	0.000524	0.147	0.185	0.00144	7.10	6.05	111
125	15.07	84.85	0.05			800	4	8.78	5.094	4.705	0.000344	0.112	0.144	0.00161	7.50	6.35	125
39	19.79	79.68	0.23			800	4	6.474	3.755	3.600	0.000237	0.087	0.112	0.00163	7.81	6.57	39
124	30.23	69.54	0.05			800	4	4.75	2.754	2.730	0.000048	0.069	0.088	0.00156	8.55	6.83	124
Copper-manganese Alloys																	
114	0.07	99.94	0.01	0.02		700	2	90.58	52.55	32.18	0.00351	0.864	0.864	0.00000	5.61	5.67	114
115	0.14	99.86	0.01	0.01		700	2	78.93	45.79	29.40	0.00309	0.784	0.819	+0.00026	5.84	5.87	115
116	0.43	99.56	0.01	0.01		700	2	50.96	29.56	22.00	0.001902	0.540	0.612	0.00074	6.24	5.86	116
117	1.05	99.05	0.01	0.01		700	2	32.88	19.07	15.84	0.001130	0.359	0.454	0.00147	6.42	6.06	117
118	1.77	98.27	0.03	0.01		700	2	21.92	12.54	11.22	0.000549	0.244	0.332	0.00198	6.64	6.25	118
119	4.55	95.34	0.06	0.02		700	2	9.63	5.887	5.446	0.000140	0.117	0.165	0.00224	7.16	6.41	119
120	9.53	90.25	0.18	0.02	C, 0.021	700	2	4.85	2.814	2.839	-0.000044	0.062	0.091	0.00258	7.52	6.77	120
121	19.82	80.03	0.09	0.02	C, 0.035	700	2	2.51	1.453	1.474	-0.000080	0.036	0.052	0.00247	8.45	7.45	121

SC = Slowly cooled in the furnace.

VSC = Furnace-cooled to and held 4 hr. at 550° C., furnace-cooled to room temperature.

TABLE 3.—*Electrical and Thermal Properties of Miscellaneous Copper Alloys*

Bar No.	Composition, Per Cent by Weight										Heat-treatment <sup>a</sup>		Elec. Cond. Per Cent. I.A.G.S. at 20° C.	Elec. Cond., $\lambda$ Ohm <sup>-1</sup> per Cm. $\times 10^{-4}$		Temp. Coef. of Elect. Resist. (20°-200° at 20° C.)	Thermal Conductivity K, Cal. per Sq. Cm. per Deg. C.		Temp. Coeff. of Thermal Exp. (20°-200° C.) at 20° C.	Wiedemann-Franz-Lorenz Ratio $\frac{K}{\lambda T} \times 10^9$		Bar No.
	Cu	Zn	Sn	Pb	Al	Fe	Ni	Mn	Other Elements	Deg. C.	Hours	20° C.		200° C.	20° C.		200° C.	20° C.		473° K		
2	99.986					0.0016			O, 0.022 S, 0.001	550	1		101.66	58.96	34.16	+0.00392	0.941	0.934	-0.00004	5.45	5.78	2
19	96.24	33.72		0.03	0.01	0.02				650	3/4		26.94	15.62	12.24	0.001591	0.287	0.349	+0.00120	6.27	6.03	19
12	96.94	3.04		0.00	0.02	0.03				700	3/4		63.12	36.67	25.21	0.002505	0.640	0.680	0.00043	5.97	5.78	12
13	95.21	4.77		0.00						700	3/4		57.00	33.062	23.31	0.002312	0.579	0.650	0.00008	5.98	5.89	13
140	97.49				0.06	0.06	0.27		Be, 2.24	815	1/2 Q		19.24	11.16	(8.645)	(0.001081)	0.205	0.249	0.00119	6.28	6.09	140
140	97.49				0.06	0.06	0.27		Be, 2.24	QR3000	2		21.99	12.760	(9.388)	(0.001268)	0.245	0.280	0.00080	6.55	5.70	140
140	97.49				0.06	0.06	0.27		Be, 2.24	815	1/2 QD		16.71	9.694	(8.184)	(0.000975)	0.177	0.221	0.00188	6.25	5.70	141
141	97.49				0.06	0.06	0.27		Be, 2.24	QRDR375	2		18.00	10.444	8.035	(0.000833)	0.196	0.240	0.00125	6.41	5.68	141
97	95.10	12.97		1.88		0.05			Be, 2.24	700	2		35.58	20.64	15.79	0.001702	0.383	0.444	0.00088	6.33	5.94	97
96	61.85	34.70		3.29		0.07				700	2		23.83	13.82	10.93	0.001467	0.258	0.317	0.00127	6.37	6.13	96
129	95.99	30.15		4.02		0.01	0.80			700	2		25.44	14.78	11.28	0.001716	0.264	0.315	0.00106	6.11	5.90	129
98	88.07	3.70	3.77	3.83	0.03	0.03	0.60			700	2		19.88	11.63	9.80	0.000860	0.215	0.276	0.00159	6.36	5.95	98
133	88.08	4.09	3.76	3.80	0.02	0.02	0.00		P, 0.25	700	2		12.21	7.082	6.304	0.000652	0.133	0.182	0.00206	6.42	6.10	133
132	60.41	37.69	1.08	1.12	0.18	0.02			Si, 0.15	Chill cast			23.38	13.56	10.22	0.001810	0.240	0.286	0.00107	6.02	5.92	132
23	64.14	17.06		0.00	0.19	0.19	18.38	0.80	C, 0.023	750	1/2		5.890	3.909	3.249	0.000357	0.080	0.100	0.00142	8.04	6.51	23
24	66.01	25.93		0.00	0.03	0.03	17.95	0.18	C, 0.020	750	1/2		5.690	3.851	3.080	0.000306	0.071	0.098	0.00217	7.41	6.72	24
25	63.79	19.79		0.00	0.14	0.14	10.29	0.18	C, 0.011	750	1/2		6.29	3.633	3.417	0.000352	0.081	0.107	0.00178	7.61	6.62	25
26	65.51	23.56		0.00	0.08	0.08	10.36	0.13	C, 0.011	750	1/2		8.53	4.947	4.590	0.000480	0.110	0.146	0.00182	7.58	6.72	26
126	69.78	29.88			0.04	0.04	10.13	0.15	Mg, 0.04	750	4		8.51	4.938	4.523	0.000495	0.101	0.135	0.00191	6.97	6.29	126
127	64.04	30.50			0.05	0.05	6.41			750	4		12.55	7.278	6.440	0.000721	0.140	0.185	0.00178	6.58	6.07	127
6	64.57	17.65	2.23	10.44	0.10	0.10	13.24			Sand cast			5.86	3.998	3.089	0.000553	0.073	0.103	0.00219	7.38	6.97	5
6	63.27	8.22	3.31	5.40	0.14	0.14	19.59	0.23		Sand cast	3Q		5.03	2.018	2.742	0.000360	0.066	0.083	0.00181	7.77	6.97	6
66	66.05				0.04	0.04	3.01		Si, 0.38	870			16.85	9.775	9.140	0.000384	0.131	0.256	0.00230	6.32	5.92	66
66A	96.05				0.04	0.04	3.01		Si, 0.38	QR500	2		35.66	20.69	16.38	0.001460	0.278	0.454	0.00112	6.23	5.85	66A
66B	96.05				0.04	0.04	3.01		Si, 0.38	870	38C		38.96	22.60	17.34	0.001681	0.403	0.487	0.00116	6.08	5.83	66B
67	89.08				5.11	5.11	4.98		Si, 0.74	850	4Q		5.85	5.135	4.755	0.000442	0.107	0.168	0.00265	7.11	7.02	67
67A	89.08				5.11	5.11	4.98		Si, 0.74	QR500	2		12.22	7.087	6.378	0.000617	0.135	0.189	0.00225	6.50	6.26	67A
67B	89.08				5.11	5.11	4.98		Si, 0.74	850	48C		12.01	6.964	6.244	0.000637	0.158	0.214	0.00197	7.64	7.25	67B
32	74.07	5.31	0.00		0.09	0.09	19.96	0.57		750	1/2		6.16	3.675	3.431	0.000230	0.092	0.116	0.00145	8.78	7.14	32
35	64.15	5.69			0.07	0.07	26.44	0.52		750			2.642	2.642	2.642	0.000128	0.068	0.086	0.00138	8.78	7.04	35
61	56.13	42.34			0.49	0.49	1.02						24.84	14.40	10.77	0.001872	0.272	0.310	0.00078	6.44	6.08	61

TABLE 3.—(Continued)

Bar No.	Composition, Per Cent by Weight								Other Elements	Heat-treatments		Elec. Cond., $\lambda$ Ohm <sup>-1</sup> per Cm. $\times 10^{-4}$	Temp. Coef. of Resist. (20°-200°) at 20° C.	Thermal Con- ductivity K, Cal. per Sq. Cm. per Cm. per Sec. per Deg. C.		Temp. Coef. of Thermal Cond. (20°- 200° C.) at 20° C.	Wiedemann- Franz-Lorenz Ratio $\frac{K}{\lambda T} \times 10^8$		Bar No.
	Composition, Per Cent by Weight									Deg. C.	Hours			20° C.	200° C.		293° K	473° K	
	Cu	Zn	Sn	Pb	Al	Fe	Ni	Mn											
49	89.38	0.00	0.38		9.41	0.52	0.31			750	3½ VSC	12.61	0.000829	0.144	0.102	0.00185	6.72	6.38	49
122	75.70	22.23			1.98	0.01				700	3	22.56	0.001310	0.240	0.208	0.00133	6.26	5.95	122
59	59.85	38.36	0.98	0.13		1.08		0.12		650	3 VSC	23.66	0.001650	0.241	0.205	0.00124	6.00	5.89	59
86	99.654			0.00		0.032				700	1	37.44	0.001541	0.304	0.487	0.00131	6.19	6.06	86
64	95.61					0.11	4.51			700		10.28	0.000140	0.111	0.176	0.00325	6.37	6.42	64
134	90.21					0.007				700	2	37.15	0.003448	0.824	0.841	0.00012	5.56	5.70	134
70	98.41		0.59			0.02				750	1½	56.44	0.002244	0.556	0.643	0.00087	5.75	5.83	70
60	72.49	17.76			4.44	1.78	3.34			650	3 VSC	10.02	0.000521	0.120	0.102	0.00195	7.05	6.45	60
7	94.00	0.00				0.08	1.03				Sand cast	2.847	0.000307	0.060	0.086	0.00230	7.19	6.74	7
72	95.69					0.16	0.99			750	1½	6.506	0.000248	0.078	0.107	0.00208	7.05	6.25	72
136	98.10	0.00	0.00	0.00	0.00	0.00	0.30			700	2	11.40	0.000530	0.129	0.175	0.00200	6.66	6.14	136
131	81.55	14.21				0.04	0.20				Chill cast	3.518	0.000433	0.068	0.096	0.00228	6.82	6.21	131
135	96.83	1.12	0.00			0.02				700	2	7.90	0.000469	0.089	0.124	0.00220	6.62	6.19	135
8A	78.30		8.04	13.32							Sand cast	9.85	0.000896	0.101	0.146	0.00247	6.04	6.27	8A
9	87.86		3.05	8.87		0.03	0.20				Sand cast	11.62	0.000711	0.129	0.171	0.00181	6.53	6.04	9
19A	88.36		1.00	0.55		0.07					Sand cast	6.369	0.000686	0.120	0.166	0.00213	6.43	6.18	19A
10	60.54	36.48	1.48		0.04	0.73	0.21				Sand cast	21.62	0.001544	0.230	0.277	0.00114	6.28	5.98	10
69	99.04			0.00		0.07				750	1½	87.02	0.002574	0.660	0.745	0.00072	5.80	5.93	69
137	50.75					48.69	0.471			800	1¼ VSC	21.24	0.002074	0.237	0.271	0.00081	6.55	6.38	137

\* All alloys, except those in the cast condition, were hot-rolled or cold-rolled from castings 2¼-in. dia., or larger, to 1¼-in. dia., annealed and cold-drawn to ½-in. dia. before final heat-treatment as stated. This was followed by air-cooling unless otherwise noted.

Q = Quenched

SC = Slowly cooled in furnace

VSC = Very slowly cooled, including holding 18 hr. at 450° C.

QR = Bar was quenched from same temperature as preceding bar and reheated at temperature stated.

QD = Cold-drawn after quenching.

*Copper-aluminum System.*—This series was studied up to 12 per cent aluminum, slightly beyond the limit of the  $\alpha$  solid solution. All the alloys were rolled and annealed at 700° or 750° C. Those alloys containing over 7 per cent aluminum were cooled very slowly to promote complete decomposition of the  $\beta$  phase.

As the composition varies across the  $\alpha$  range, the conductivity decreases, although not nearly as rapidly as in the silicon series; and the

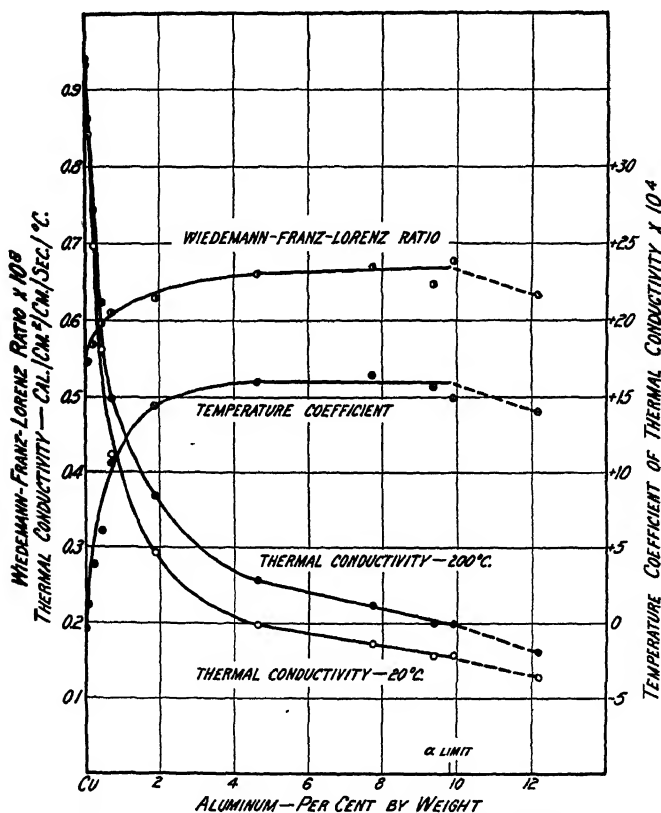


FIG. 2.—THERMAL CONDUCTIVITY OF COPPER-ALUMINUM ALLOYS IN  $\alpha$  SOLID SOLUTION RANGE.

Lorenz ratio and temperature coefficient increase rapidly at first and then remain practically constant. The appearance of the  $\delta$  phase beyond 10 per cent aluminum causes a decrease in conductivity, in temperature coefficient, and in Lorenz ratio.

*Copper-nickel System.*—To insure sound castings, all these alloys were deoxidized with magnesium, a small amount of which remained, as shown by the analyses. Manganese was present in the commercial alloys. The alloys were cold-rolled with intermediate annealings, and finally were given a drastic annealing at 800° C. to render them homogeneous.

The measurements are summarized in Table 2 and Fig. 3. The behavior is quite normal for a series of solid solutions, although the very high Lorenz ratio at 20° C. for the high-nickel alloys is to be noted. Fig. 4 shows on a larger scale the alloys up to 10 per cent nickel.

*Copper-manganese Series.*—These alloys also were deoxidized with magnesium. The castings were hot-rolled and given a final homogenizing

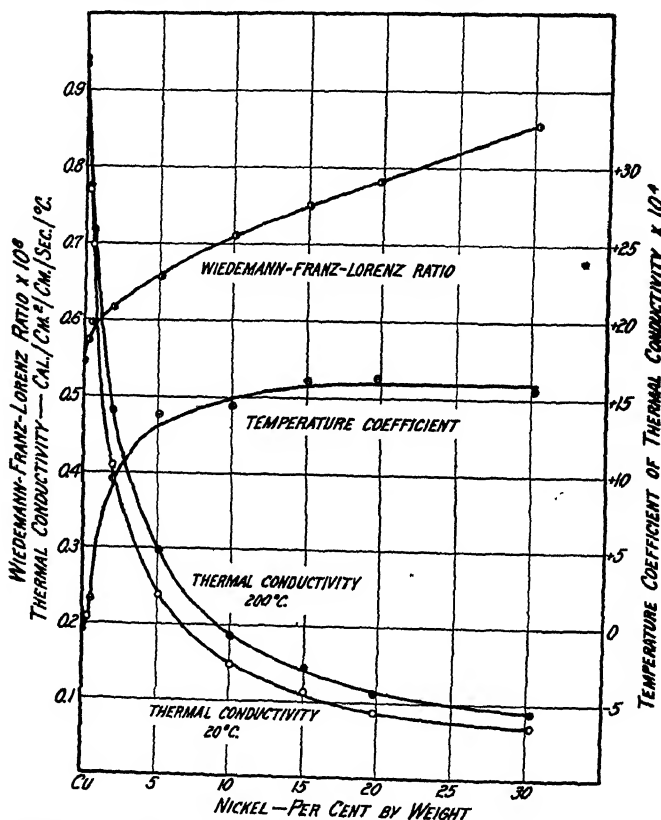


FIG. 3.—THERMAL CONDUCTIVITY OF COPPER-NICKEL ALLOYS (0 TO 30 PER CENT NICKEL).

anneal at 700° C. The results, plotted in Figs. 5 and 6 and tabulated in Table 2, show again the behavior characteristic of solid solution series. The conductivity reaches lower values than in any other binary series examined, and the Lorenz ratio approaches the high values reached in the copper-nickel system.

*Miscellaneous Alloys.*—Table 3 lists all alloys that do not fall in the binary series previously considered. Most of these alloys were fully annealed after extensive working, and slowly cooled where this was necessary. A few were given special heat-treatments for precipitation-hardening as listed. A few alloys were tested in the sand-cast condition;

and two, which find some application as die-casting alloys, were in the form of 1-in. diameter chill castings, machined to 0.750-in. diameter for test.

In using these results, particularly those for commercial alloys of three or more components, the possible effect of change of composition from the

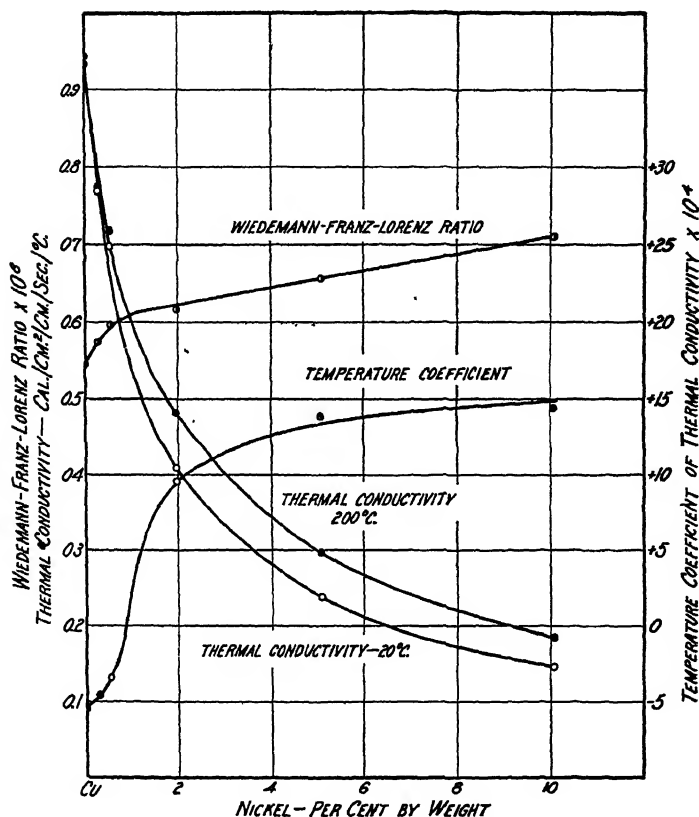


FIG. 4.—THERMAL CONDUCTIVITY OF COPPER-NICKEL ALLOYS (0 TO 10 PER CENT NICKEL).

nominal one and the effect of impurities must be considered. The figures given are representative of alloys of the composition given, and for the stated heat-treatment only.

#### RELATION BETWEEN THERMAL AND ELECTRICAL CONDUCTIVITY

Many attempts have been made to establish a connection between the conductivities of metals for heat ( $K$ ) and electricity ( $\lambda$ ). It has long been known that the Wiedemann-Franz ratio,  $\frac{K}{\lambda}$ , is approximately a constant for several metallic elements at a given temperature, and that the Lorenz

factor,  $\frac{K}{\lambda T}$ , is very nearly a constant for a given metal or alloy over a fairly wide temperature range (not approaching absolute zero) and does not widely vary for different metals. Griffiths and Schofield<sup>7</sup> found that the Lorenz factor was approximately constant for a group of aluminum

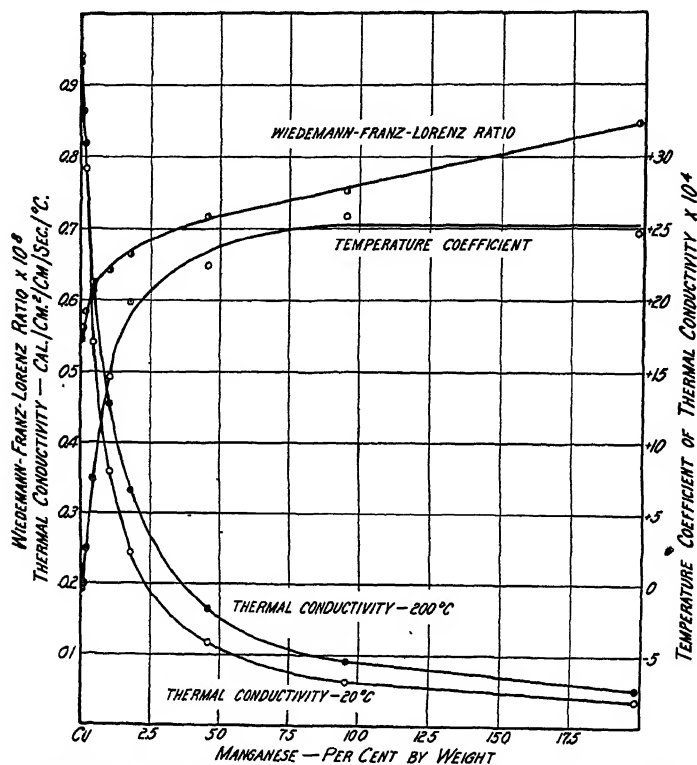


FIG. 5.—THERMAL CONDUCTIVITY OF COPPER-MANGANESE ALLOYS (0 TO 20 PER CENT MANGANESE).

alloys of various compositions, but differed from that for pure aluminum; and that it was approximately constant for some aluminum bronzes but differed from that for copper. Obviously the ratio must depend upon the composition of the alloy and somewhere intermediate values must occur. The solid solutions of copper studied in the present investigation show that in every case the Lorenz coefficient increases very rapidly on the first additions of a solute atom to the copper lattice, and that later additions have much less effect, the curve of the Lorenz ratio against composition showing a marked change of slope at a point that varies with the element added.

A constant value of the Wiedemann-Franz ratio means, of course, that a straight line intersecting the origin would result from plotting values of  $K$  against the corresponding values of  $\lambda$  at a given temperature. That

this does not happen is obvious from the wide variation of the ratio. However, all the results for all the copper alloys that have been investigated do lie on a single curve, not passing through the origin, when plotted in this way.\* Fig. 7 shows every experimental point obtained in the

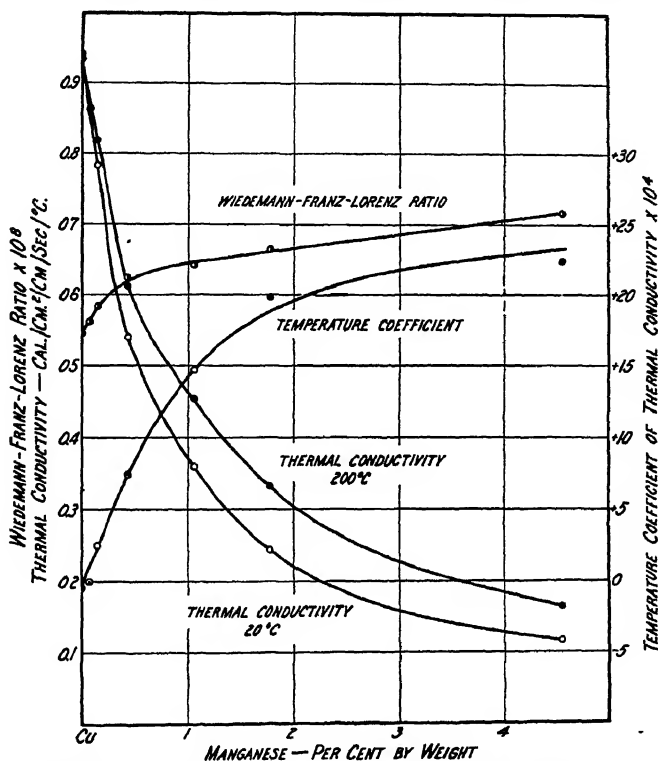


FIG. 6.—THERMAL CONDUCTIVITY OF COPPER-MANGANESE ALLOYS (0 TO 5 PER-CENT MANGANESE):

present investigation, at 20° and at 200° C. Each series forms a curve which at low conductivities is a straight line intersecting the thermal conductivity axis at a small but definite value that is the same for both temperatures, while at high conductivities there is appreciable curvature. If the thermal conductivity is plotted against the product of the corresponding electrical conductivity and absolute temperature ( $\Delta T$ ), as in Fig. 8, all the values at both temperatures for all alloys fall practically upon a single curve.

The spread of the experimental points around the mean curve is somewhat greater than the supposed experimental error, but there is little regularity in the deviation, and much higher accuracy would be needed before differentiation of the various systems would be warranted. This

\* Hume-Rothery (The Metallic State, Oxford, 1931) drew a curve of this type for the copper-nickel alloys and showed it to be approximately a straight line.



agreement is remarkable when it is considered that, in addition to the homogeneous face-centered-cubic  $\alpha$  solid solutions that constitute the bulk of the alloys there are included  $\beta$  brass (body-centered-cubic), a copper-iron alloy consisting of long fibers of iron in a copper matrix, and various precipitation-hardened alloys.

The curve is approximately straight for over half its length. This is in accordance with the simple theory that thermal conductivity is composed

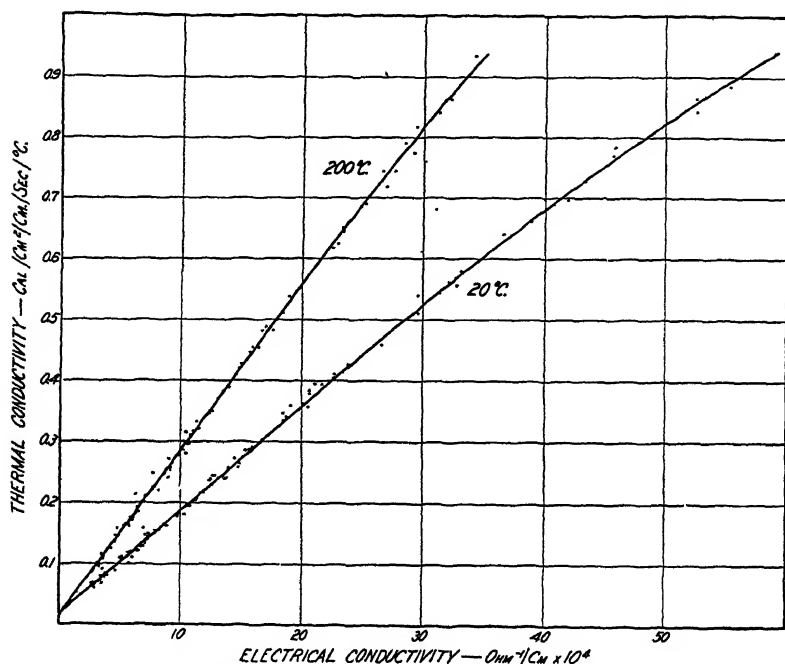


Fig. 7.—COMPARISON OF ELECTRICAL AND THERMAL CONDUCTIVITIES AT 20° AND 200° C. OF ALL ALLOYS MEASURED.

of a metallic (electronic) and a nonmetallic part, and that the Lorenz law holds exactly for the metallic part; i.e.:

$$K = c\lambda T + k$$

where  $K$  is the total thermal conductivity;  $k$  the nonmetallic part;  $\lambda$  the electrical conductivity;  $T$  the absolute temperature, and  $c$  a constant, which may be considered as a true Lorenz ratio for the metallic part of the conductivity. Values read from Fig. 8 are  $k = 0.018$  and  $c = 5.71 \times 10^{-9}$  c.g.s. units.  $k$  would not vary much for the  $\alpha$  solid solutions of copper, but it is surprising that  $\beta$  brass and the other alloys of different structure fall so closely on the curve.

The change of the conductivities with temperature is as closely in accordance with the curve as the change with composition, even though the causes are so different. The measurements of Schofield<sup>8</sup> for pure cop-

per at temperatures up to 625° C. fall closely on the curve, and also the values of Lees<sup>7</sup> for brass, manganin and German silver at temperatures between 18° and -170° C. The values for copper at temperatures below atmospheric as reported by Lees, Meissner<sup>8</sup>, and Gruneisen and Goens<sup>10</sup> provide a smooth extrapolation of the curve with ever decreasing slope.

Although this curve is based on alloys, usually solid solutions, containing over 50 per cent of copper, many of the other elements and

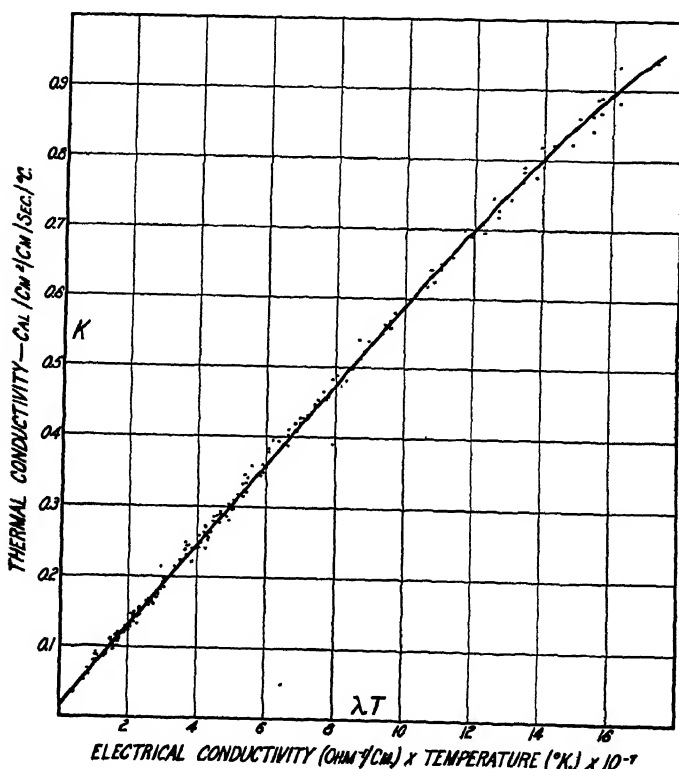


FIG. 8.—RELATION OF THERMAL CONDUCTIVITY AND PRODUCT OF ELECTRICAL CONDUCTIVITY AND ABSOLUTE TEMPERATURE OF COPPER ALLOYS.

alloys fall exactly on or very near to it. In practically every case the most reliable determinations for the metallic elements lie much nearer to the  $K$  vs.  $\lambda T$  curve of Fig. 8 than they do to the line representing a constant Lorenz ratio. Lees' figures for silver, zinc, cadmium, and nickel are almost exactly on the curve, those for iron are above it. Schofield's figures for magnesium, zinc and nickel are very slightly below. The values as given by Smith<sup>11</sup> for lead, thallium, tin, cadmium, zinc, magnesium, and the binary alloys of most of these all fall on a single straight line, slightly below that of Fig. 8 and of slightly less slope—a difference that may be due to the fact that there is a difference of 38° K in

the temperatures at which  $K$  and  $\lambda$  were measured. Aluminum seems to be definitely abnormal. At room temperature, the conductivities of most of its alloys, except those containing silicon, lie very near a straight line,\* but the values of  $k$  and  $c$  are approximately 0.05 and  $4.65 \times 10^{-9}$  respectively. The variation of the conductivities with temperature is not

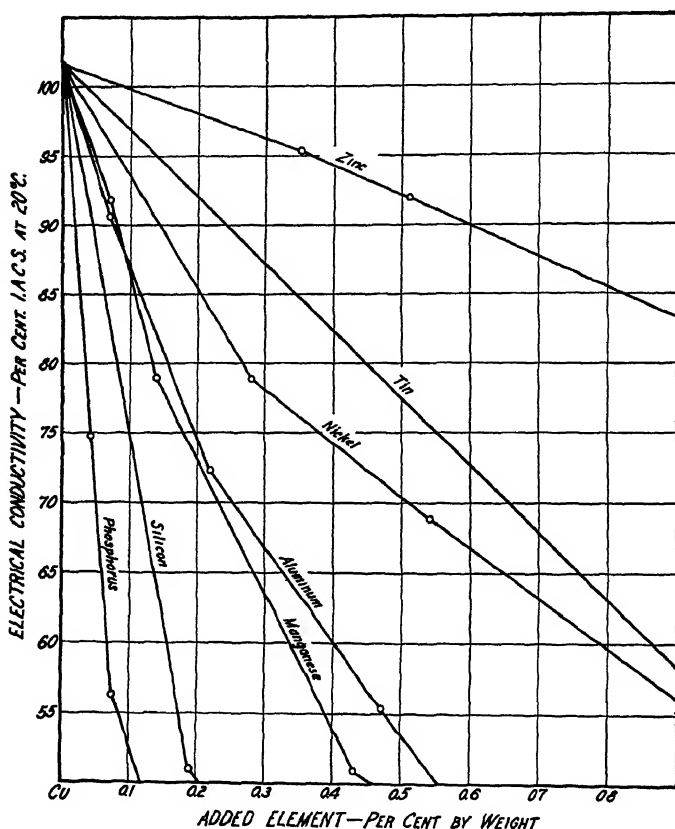


FIG. 9.—EFFECT OF SOME ELEMENTS ON ELECTRICAL CONDUCTIVITY OF COPPER AT 20° C.

in accordance with the usual relation, in that the thermal conductivity increases with increase of temperature, whereas that of most other metallic elements decreases. For example, Schofield's results for pure aluminum (99.7 per cent) over a range of temperatures give a short line almost at right angles to the  $K$  vs.  $\lambda T$  line for the alloys at one temperature.

In view of the tedious and rather uncertain nature of thermal conductivity measurements, and the ease and accuracy of electrical deter-

\* The measurements of Masumoto<sup>12</sup> lie almost perfectly on a straight line. Griffiths and Schofield's values and thirteen unpublished measurements of the present authors, lie very close to it. Mannchen's<sup>13</sup> results show rather more scatter.

minations, the practical value of the curves given in Figs. 7 and 8 is obvious. The thermal conductivity of a copper alloy can be read with confidence from these curves, with an accuracy of at least 0.02 cal. per cm. per sec. For most alloys the value obtained will be more precise than this—even more precise than can be measured with any but the most refined apparatus and technique. To facilitate the conversion the table in Appendix B has been compiled. It shows at a glance the approximate thermal conductivity to be expected of an alloy of a given electrical conductivity, expressed as a percentage of the International Annealed Copper Standard at 20° C.

It is probable that similar curves and tables could be constructed for the alloys of other elements if a sufficient number of accurate determina-

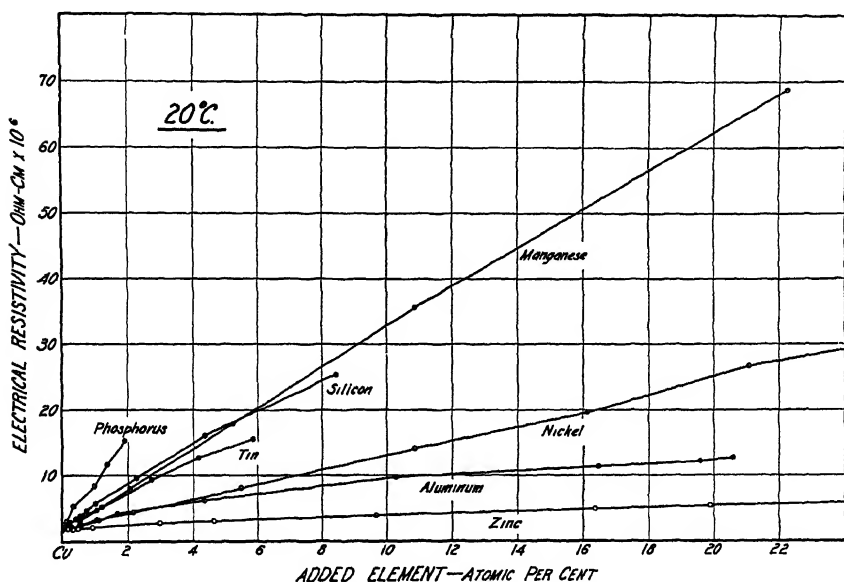


FIG. 10.—ELECTRICAL RESISTANCE OF SOME  $\alpha$  SOLID SOLUTION ALLOYS OF COPPER AT 20° C.

tions were available, but at present this is difficult except for aluminum and possibly iron.

#### EFFECT OF ELEMENTS ON ELECTRICAL CONDUCTIVITY OF COPPER

The results of this study provide interesting data on the effect of impurities or intentionally added elements on the electrical conductivity of copper. In Fig. 9 the results for the binary series are plotted to show the variation of electrical conductivity (per cent I.A.C.S.) with weight per cent of added element. In Figs. 10 and 11 the resistance is plotted against atomic per cent solute, which gives a series of approximately straight lines. There is a considerable difference in the effectiveness of

the different elements in reducing the conductivity, phosphorus being the most and zinc the least powerful of the elements studied.

### SUMMARY

The thermal and electrical conductivities at 20° and 200° C. have been determined for the binary alloys of copper with silicon, aluminum, manganese and nickel, and for a large number of ternary and more complex commercial alloys. In the binary alloys, as the amount of added element increases in the  $\alpha$  solid solution range the conductivities decrease and the Lorenz ratio increases, at first rapidly and then more slowly.

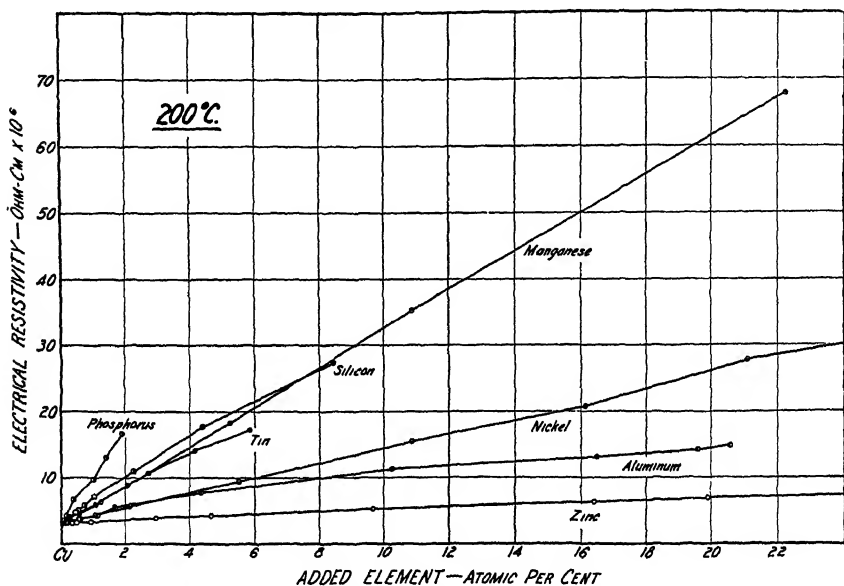


FIG. 11.—ELECTRICAL RESISTANCE OF SOME  $\alpha$  SOLID SOLUTION ALLOYS OF COPPER AT 200° C.

The thermal conductivity of the alloys increases with temperature, although that of pure copper decreases.

The ratio between electrical and thermal conductivity varies considerably, but it is shown that all the results at both temperatures for all copper alloys (including those for the binary series with tin, zinc and phosphorus previously published) lie on a single curve when the thermal conductivity is plotted against the product of the electrical conductivity and the absolute temperature. This curve is almost a straight line and intersects the thermal conductivity axis at a small but definite value. The results of all the alloys measured lie much closer to this curve than to any curve of constant Lorenz ratio. Alloys of other metals probably lie on similar curves.

## ACKNOWLEDGMENTS

This research was started in 1928 at the suggestion of the late Mr. W. H. Bassett, Metallurgical Manager of The American Brass Co. The authors wish to acknowledge their sincere gratitude to him for his genuine interest and encouragement, which greatly aided the prosecution of the research in its initial stages. Thanks are also due to Mr. H. C. Jennison, who encouraged the completion of the research according to the original plans.

Many of the earlier measurements were made by Mr. W. E. Lindlief and Mr. E. L. Munson, whose assistance the authors gratefully acknowledge.

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APPENDIX A.—ELECTRICAL CONDUCTIVITY AND LORENZ RATIO AT 200° C. FOR ALLOYS REPORTED IN PREVIOUS PAPERS<sup>1,2</sup>

Bar No.	Electrical Conductivity at 200° C., $\text{Ohm}^{-1} \text{Cm}^{-1} \times 10^{-4}$	Temperature Coefficient of Electrical Resistance 20°-200° C.	Lorenz Ratio $\frac{K}{\lambda T} \times 10^8$ 200° C.
Copper-zinc Alloys			
2	34.16	0.00392	5.78
90	33.08	0.00372	5.68
89	32.82	0.003595	5.71
73	30.14	0.003235	5.76
12	25.21	0.002505	5.78
13	23.31	0.002312	5.89
14	18.94	0.001860	6.00
15	15.65	0.001573	6.01
16	14.44	0.001540	5.98
18	12.51	0.001484	5.90
21	12.00	0.001540	5.98
22	12.30	0.001980	5.93
88	13.49	0.002868	5.98
85	14.76	0.003398	6.00
Special Brasses			
52	18.41	0.001839	5.86
54	11.37	0.001615	5.98
55	14.57	0.001559	5.93
56	11.50	0.001344	5.99
57	11.43	0.001804	5.91
Copper-tin Alloys			
74	22.51	0.002178	5.79
75	16.67	0.001492	6.10
41	9.30	0.000822	6.00
43	7.080	0.000637	6.24
44	5.822	0.000581	6.21
40	6.616	0.000590	6.27
42	9.248	0.000848	6.03
Copper-phosphorus Alloys			
93	28.38	0.002198	5.89
82	23.32	0.002218	5.87
95	14.94	0.001330	6.03
83	10.28	0.000843	6.14
94	7.715	0.000646	6.79
84	6.004	0.000503	6.26

APPENDIX B.—TABLE FOR APPROXIMATE CONVERSION OF THERMAL AND  
ELECTRICAL CONDUCTIVITIES OF COPPER-BASE ALLOYS AT 20° C.

(Based on Fig. 7)

Electrical Conductivity, Per Cent I.A.C.S. at 20° C.	Thermal Conductivity, Cal. per Sq. Cm. per Cm. per Sec. per Deg. C. at 20° C.									
	0	1	2	3	4	5	6	7	8	9
0	0.018	0.028	0.038	0.047	0.057	0.067	0.077	0.086	0.096	0.106
10	0.116	0.126	0.136	0.146	0.156	0.166	0.176	0.186	0.195	0.205
20	0.215	0.225	0.235	0.245	0.255	0.265	0.275	0.285	0.294	0.304
30	0.314	0.324	0.334	0.343	0.353	0.363	0.373	0.382	0.392	0.402
40	0.411	0.421	0.431	0.440	0.450	0.460	0.470	0.479	0.489	0.499
50	0.508	0.518	0.528	0.537	0.547	0.556	0.565	0.574	0.584	0.593
60	0.602	0.611	0.620	0.629	0.638	0.647	0.656	0.665	0.674	0.682
70	0.691	0.699	0.708	0.716	0.724	0.733	0.741	0.749	0.757	0.766
80	0.774	0.782	0.790	0.798	0.806	0.814	0.821	0.829	0.837	0.845
90	0.852	0.860	0.867	0.875	0.882	0.890	0.897	0.905	0.912	0.920
100	0.927	0.934	0.941	0.949	0.956					

*Conversion Factors*

Elect. Cond. (per cent I.A.C.S.) = Elect. Cond. ( $\text{ohm}^{-1}\text{-cm.}^{-1}$ )  $\times 1.724 \times 10^{-4}$

$$= \frac{1.724 \times 10^{-4}}{\text{Elect. Resist. (ohm-cm.)}}$$

Thermal Cond., Watts/cm.<sup>2</sup>/cm./°C. = Cal/cm.<sup>2</sup>/cm./sec./°C.  $\times 4.186$

B.t.u./ft.<sup>2</sup>/in./sec./°F. = Cal/cm.<sup>2</sup>/cm./sec./°C.  $\times 0.8064$

B.t.u./ft.<sup>2</sup>/in./hr./°F. = Cal/cm.<sup>2</sup>/cm./sec./°C.  $\times 2903$ .

B.t.u./ft.<sup>2</sup>/ft./hr./°F. = Cal/cm.<sup>2</sup>/cm./sec./°C.  $\times 241.9$



## Recrystallization and Grain Growth in Cold-worked Polycrystalline Metals\*

By L. W. EASTWOOD,† MEMBER A.I.M.E., ARTHUR E. BOUSU,‡ AND C. T. EDDY,§  
ASSOCIATE MEMBER A.I.M.E.

(New York Meeting, February, 1935)

THE recrystallization and grain-growth phenomena of cold-worked metals have considerable industrial importance because of their role in the fabrication of metals. For this reason, and because of the general academic interest in the subject, these processes have received considerable attention since the time of J. E. Stead's paper<sup>1</sup> on The Crystalline Structure of Iron and Steel. There are considerable differences of opinion regarding the theory of recrystallization and grain growth and also differences in the observation of the *modus operandi* of the processes themselves. The value of many of the existing quantitative data on grain growth is decreased by the failure to distinguish between the grain sizes just after complete recrystallization and those resulting from coalescence. For this reason also, the value of the diagrams of stable grain sizes, like those produced by Bass and Glocker<sup>2</sup> and Czochralski<sup>3</sup>, is lessened in so far as an interpretation of the facts of recrystallization is concerned. It is hoped that the data presented in this paper will help to clarify and to simplify the facts relating to recrystallization, and at the same time will show that some of the present-day conceptions are untenable. A paper on the theory of recrystallization, with additional data, will be completed in the near future by the writers.

Since the literature on the subject has been adequately and frequently reviewed, the only references to it in this paper will be those necessary in the discussion of the data presented.

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\* This paper reports a portion of a research project carried on in the metallurgical laboratories of the Michigan College of Mining and Technology and submitted to the faculty of the College by Mr. Bousu in partial fulfillment of the requirements for a Master of Science degree in Metallurgy. Manuscript received at the office of the Institute Feb. 6, 1935.

† Assistant Professor of Metallurgy, Michigan College of Mining and Technology, Houghton, Mich.

‡ Graduate student in Metallurgy, Michigan College of Mining and Technology.

§ Associate Professor of Metallurgy, Michigan College of Mining and Technology.

<sup>1</sup> J. E. Stead: *Jnl. Iron and Steel Inst.* (1898) **53**, 145-205.

<sup>2</sup> Bass and Glocker: *Ztsch. f. Metallkunde* (1928) **20**, 179-183.

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It is first necessary to define recrystallization, coalescence and recrystallization temperature. These definitions are presented here for the purpose of precise terminology; no new concepts are involved, and certainly no criticism of former definitions is implied. When an alpha brass, for example, is reduced cold by 15 per cent of its original thickness and then annealed at 450° C., new grains begin to form and grow, mainly at the expense of the deformed metal and perhaps also at the expense of some of the newly formed grains. After a certain length of time the last of the old, deformed metal has just disappeared. Further heating at 450° C. causes coarsening; i.e., disappearance of some of the newly formed, unstrained grains. In this paper the process of replacement of the strained material by unstrained grains is called recrystallization, and the process of absorption of one unstrained grain by another after recrystallization is complete is called coalescence. During coalescence, one grain grows and the other gradually diminishes in size and disappears. Hence coalescence is not, like the coalescence of two drops of water, a bodily absorption of one grain by another. Either recrystallization or coalescence may be involved in grain growth, depending on whether the grains grow at the expense of the deformed metal or by absorption of unstrained grains after the disappearance of the cold-worked crystals. However, it should be noted that some of the newly formed, unstrained grains may be absorbed before the complete disappearance of the strained metal. For the sake of exactness of terms, the recrystallization process may be said to end and coalescence to begin with the last disappearance of the cold-worked grains. The recrystallization temperature frequently is defined as the minimum temperature at which the newly formed grains can be observed under a high-powered microscope. Such a definition is unsatisfactory, however, since this temperature is the minimum recrystallization temperature of only a very few isolated portions of the metal. In this paper the recrystallization temperature of a given uniformly cold-worked metal is defined as the minimum temperature at which all of the cold-worked metal just disappears after annealing for a given fixed time. As is well known, this recrystallization temperature depends upon the kind and composition of the metal and is increased by: (1) decreased cold deformation, (2) decreased time at the annealing temperature, (3) increased grain size of the original piece, (4) increased quantity of a foreign obstruction material, and (5) increased temperature of the cold deformation.

#### EXPERIMENTAL PROCEDURE

In order that the grain sizes just after complete recrystallization could be distinguished from those produced by coalescence, 1-in. flat tensile bars of 66-34 alpha brass were tapered to  $\frac{3}{8}$  in. at the center, annealed

by a high temperature to give a coarse grain size (0.60 mm.), and then broken in tension. By this method a specimen about 5 in. long was obtained, which had a general strain gradient of 0 to about 36 per cent reduction in area by drawing. The percentage of reduction in area along the bar was determined by means of a micrometer caliper. After the Rockwell E hardnesses along the bars were obtained, the bars were

TABLE 1.—*Grain Sizes and Heat-treatments of Bars*

Sample No.	Heat-treatment		Recrystallization		Grain Size, Mm							Rockwell E Hardness at Complete Recrystallization
	Temp, Deg C	Time, Min.	Begins at Per Cent Deformation	Complete at Per Cent Deformation	At Complete Recrystallization	5 Per Cent	10 Per Cent	15 Per Cent	20 Per Cent	25 Per Cent	30 Per Cent	
1	700	5	5.8	16.0	0.080		0.080	0.080	0.075	0.055	0.045	57.1
2	700	15	3.8	6.5	0.200	0.200	0.135	0.095	0.095	0.095	0.090	48.1
3	700	30	3.3	5.5	0.250	0.250	0.150	0.150	0.120	0.120	0.120	47.2
4	700	60	3.0	5.0	0.300	0.300	0.150	0.150	0.150	0.150	0.150	42.5
5	700	180	2.0	3.5	0.400	0.300	0.200	0.175	0.175	0.175	0.175	38.8
6	700	900		3.3	0.400	0.400	0.250	0.250	0.250	0.250	0.250	36.2
7	600	5	12.0	36.0	0.035			0.035	0.035	0.035	0.035	
8	600	15	6.5	17.0	0.090		0.090	0.090	0.070	0.060	0.060	59.0
9	600	30	6.0	13.0	0.110		0.110	0.090	0.075	0.065	0.065	56.3
10	600	60	5.3	12.5	0.150	0.150*	0.150	0.110	0.090	0.075	0.075	55.0
11	600	180	5.0	7.2	0.220	0.220	0.125	0.120	0.110	0.090	0.090	51.0
12	600	900	4.0	7.0	0.250	0.250	0.220	0.125	0.120	0.110	0.110	48.0
13	500	5	25.0	none						0.010	0.010	
14	500	15	12.1	21.0	0.065			0.065	0.065	0.055	0.040	70.0
15	500	30	9.6	20.5	0.075		0.075	0.075	0.070	0.060	0.055	62.7
16	500	60	9.0	19.5	0.075		0.075	0.075	0.075	0.070	0.065	61.0
17	500	180	7.9	15.5	0.080		0.080	0.080	0.080	0.075	0.070	57.4
18	500	900	7.0	12.0	0.180		0.160	0.090	0.080	0.075	0.070	55.1
19	500	2700	5.0	10.0	0.160	0.160	0.160	0.080	0.075	0.075	0.075	54.5
20	450	15	15.7	36.0	0.035				0.035	0.035	0.035	
21	450	30	12.4	25.5	0.050			0.050	0.050	0.050	0.050	66.6
22	450	60	12.0	24.0	0.065			0.065	0.065	0.065	0.050	65.1
23	450	180	9.8	22.0	0.075		0.075	0.075	0.075	0.070	0.065	61.3
24	450	2700	7.8	17.0	0.090		0.090	0.090	0.075	0.075	0.070	58.1
25	400	15	20.0	none							0.015	
26	400	30	19.5	none						0.020	0.020	74.1
27	400	60	15.6	32.0	0.035				0.035	0.035	0.035	73.9
28	400	180	13.4	29.0	0.040				0.040	0.040	0.040	61.9
29	400	900	11.5	22.0	0.080			0.080	0.080	0.060	0.040	62.5
30	400	2700	9.7	19.5	0.080			0.080	0.080	0.065	0.040	
31	300	1120	23.3	none							0.010	
32	300	2820	20.0	none							0.015	

\* 6 per cent.

annealed at various times and temperatures and the Rockwell hardnesses again determined. These hardness readings were used as a check on the determination of the positions of the regions where recrystallization began and where it was just complete as determined by microscopical examination. For annealing, the specimens were always placed in a furnace that previously had been heated to the desired temperature.

There was one specimen for each heat-treatment, thus making it unnecessary to use the same specimen for various heat-treatments with intervening microscopical examination. The long edge of the specimen was polished, etched, examined, and photographed at each 5 per cent reduction and at other pertinent spots. In order to check the results obtained

TABLE 2.—*Grain Sizes and Heat-treatments of Bars*

Sample No.	Heat-treatment		Recrystallization		Grain Size, Mm.									
	Temp, Deg. C.	Time, Min	Begins at Per Cent Deformation	Complete at Per Cent Deformation	At Complete Recrystallization	5 Per Cent	10 Per Cent	15 Per Cent	20 Per Cent	25 Per Cent	30 Per Cent	35 Per Cent	40 Per Cent	
A	850	2 5	8 0	20 0	0 060		0.060	0.060	0 060	0 040	0 035	0 027	0 022	
B	850	5	4 0	12.0	0.100	0 100	0.100	0 060	0 060	0 060	0 055	0 055	0 050	
C	850	20	3 0	8 5	0.105	0 105	0.105	0.100	0 095	0 095	0 090	0 080	0 075	
D	850	60		7 0	0 125	0 125	0.125	0 120	0 115	0 110	0 110	0 105	0 105	
E	850	180		5 5	0.250	0 250	0 200	0 200	0 200	0 200	0 175	0.160	0.150	
F	850	900		3 0	0 430	0 350	0 200	0.200	0 200	0 200	0 175	0 160	0.160	
G	700	3 5	20 0	none						0 013	0.013	0 013	0 013	
H	700	5	10 0	25 0	0.040		0.040	0.040	0 040	0 040	0 035	0 030	0 022	
I	700	20	9 5	15 0	0 0675		0 0675	0.0675	0 055	0 050	0 040	0 032	0 030	
J	700	60	5 0	12 5	0 088		0 088	0.085	0 065	0 050	0 045	0 040	0 035	
K	700	180	5 0	13 0	0 105	0.105	0 105	0 085	0 075	0 070	0 060	0 055	0 050	
L	700	900	1.7	5 0	0 150	0 150	0 105	0.090	0 075	0 075	0 075	0 075	0 075	
M	700	1140		2 5	0 400	0 300	0 150	0 105	0 085	0 120	0 100	0 080	0 080	
N	600	5	16 9	41 0	0 0125				0.0125	0.0125	0.0125	0.0125	0.0125	
O	600	20	12 5	22 0	0 045			0 045	0.045	0 045	0 035	0.030	0 017	
P	600	60	7.4	15 0	0 050		0 050	0 050	0.045	0.045	0 035	0.030	0.022	
Q	600	180	6 5	11 5	0 075	0 075	0 075	0 075	0 065	0 050	0 045	0 035	0 025	
R	600	900	4 2	10 0	0.100	0 100	0 075	0 070	0 065	0 050	0 037	0 035		
S	600	2340		2 0	0 450	0 450	0 200	0 150	0 100	0 070	0.065	0.050	0 040	
T	500	20	19 0	none					0 0125	0.0125	0.0125	0.0125	0.0125	
U	500	60	16 2	35 0	0 0175				0 0175	0.0175	0.0175	0.0175	0 015	
V	500	180	15 0	28 0	0 030			0 030	0 030	0 030	0 025	0 022	0.020	
W	500	900	12 5	25.0	0 0325			0 0325	0 0325	0 0325	0 030	0.027	0.027	
X	500	2880	5 0	15 0	0 075		0 075	0 075	0 040	0 040	0 032	0 032	0 032	
Y	500	5000	5.0	15 0	0 080		0 080	0 080	0 065	0 055	0 052	0 035	0.030	
Z	400	60	25 0	none							0 0075	0.0075	0.0075	
AA	400	180	20 0	none					0 010	0.010	0.010	0 010	0 010	
BB	400	900	17 5	37.0	0 010				0 010	0 010	0.010	0 010	0 010	
CC	400	3710	13 0	26 0	0.032			0 032	0 032	0 032	0 024	0.022	0.020	
DD	400	9600	12 0	20 0	0 060			0 060	0 060	0 0525	0.035	0 0325	0 0275	

<sup>a</sup> 7 per cent.

from the drawn bars, wedges of an 89-11 alpha brass were machined and annealed at a high temperature to produce coarse grains and these specimens were then cold-rolled. Thus, specimens were produced that were about 5 in. long and had a general strain gradient of 0 to 45 per cent reduction in thickness by rolling. These were given treatments similar to those given the drawn bars. The grain sizes and heat-treatments of these two sets of bars are given in Tables 1 and 2.

## DISCUSSION OF RESULTS

Specimens with a general strain gradient have the advantage of containing all degrees of deformation, and thus make it possible to study readily the effects of various degrees of strain. Such bars also permit the accurate identification of and distinction between the old, strained grains and the newly formed, unstrained ones. Furthermore, for a given time at a definite temperature that is equal to or above the recrystallization temperature of that portion of the bar having the highest deformation, there is one degree of strain at which recrystallization is complete, the grains at this point being unaltered by subsequent coalescence. It might be argued that the general strain gradient allows a different mechanism of growth by permitting the newly formed grains to absorb adjacent deformed metal and thus causing the crystallization to proceed toward the low deformation end of the bar with the development of abnormal grain sizes. That this is impossible is evident from the following consideration of the mechanism of crystallization of such test pieces.

When a bar  $4\frac{1}{2}$  in. long containing a deformation gradient of 0 to 40 per cent is annealed, the new grains form first at the regions of the highest reduction; slightly later new grains also begin to form at lower deformation. For example, after a definite time at a certain temperature new grains may be observed to form at a deformation as low as 12 per cent. These new grains are surrounded by unrecrystallized material, and their number increases toward the end of highest deformation until at 22 per cent deformation the recrystallization is complete. From this point to the region of 40 per cent reduction the bar will be completely recrystallized. Coalescence will have occurred in that portion of the bar having the greater degree of deformation, but no coalescence will have occurred at the point of complete recrystallization. Thus any given portion of the bar, such as that which has just become completely recrystallized, is adjacent to regions on the lower deformation side that are almost completely recrystallized. Likewise, on the other side, the portion of the bar that has just become completely recrystallized is adjacent to a completely recrystallized area in which the grains are practically the same size as those at the portion just completely recrystallized. Thus, a general strain gradient under these conditions cannot and does not give rise to "germinant" grains or "abnormal" grain growth, as has been frequently contended. This conclusion is attested by the fact that Mathewson and Phillips<sup>4</sup> obtained data on uniformly strained alpha brass which check these results quantitatively, though these investigators did not study the grain sizes just after complete recrystallization. Furthermore, the writers have used a coarse-grained

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<sup>4</sup> C. H. Mathewson and A. Phillips: *Trans. A.I.M.E.* (1916) **54**, 608-670.

66-34 alpha brass, which had been reduced uniformly by cold-rolling 5, 10 and 30 per cent. When these uniformly strained pieces were annealed to cause just complete recrystallization without coalescence, the resulting grain sizes for the three degrees of deformation lay on the curve of Fig. 1a. This shows that the recrystallization of the uniformly strained material is exactly like that which occurs in the regions having the same degree of reduction in the general strain-gradient bars.

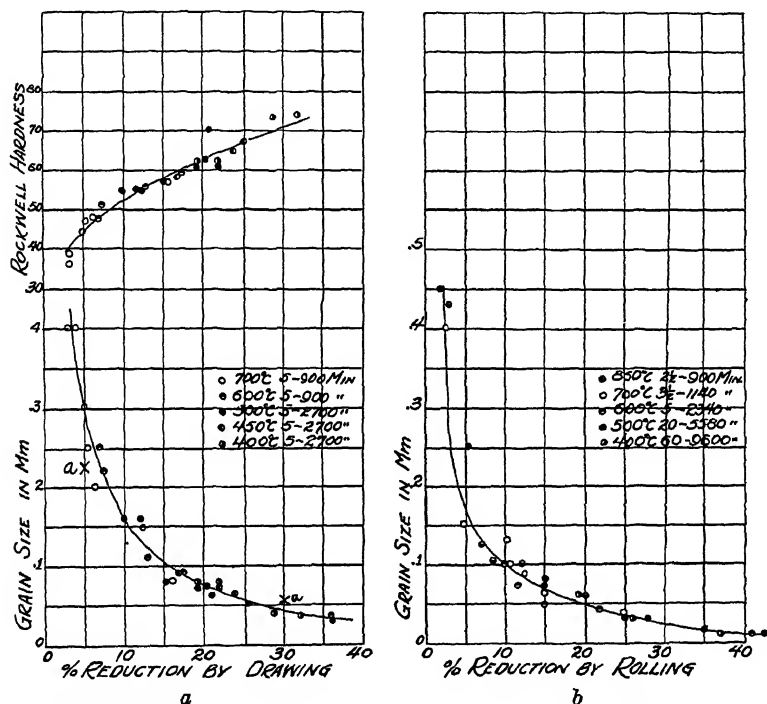


FIG. 1.—PERCENTAGE OF DEFORMATION PLOTTED AGAINST GRAIN SIZE OF REGION AT WHICH RECRYSTALLIZATION IS JUST COMPLETE.

When the percentage of deformation is plotted against the grain size of the region at which recrystallization is just complete, the uniform curves of Fig. 1 are obtained. These curves show that the grain size of the completely recrystallized alpha brass is independent of both time and temperature providing coalescence has not occurred, but is dependent only upon the degree of deformation. This relationship is clearly established for two different kinds of alpha brass, one deformed by cold-drawing and the other reduced by cold-rolling. Fig. 1a also shows the Rockwell E hardnesses of the just completely recrystallized regions for the various degrees of deformation.

In the light of this relationship, it is evident that the now classical examples of grain growth represented by Chappell's tapered bar and by

Sauveur's bent bar and Brinell impressions do not represent coarse crystals formed by "germinant" grains, the growth of which is favored by a "critical strain" at a "germinant temperature," as has been postulated. Rather, such coarse grains are part of ordinary normal recrystallization. The large crystals are coarse because the degree of deformation is low with the consequent formation of few nuclei which grow only at high temperatures. They cannot be ascribed to coalescence of surrounding grains by large grains called germinant grains. If this explanation were true, it would be difficult, as it was for H. M. Howe<sup>5</sup>, to understand why the small grains existing in contact with the large germinant grains were not entirely or at least partly absorbed with the development of columnar grains when Sauveur prepared his recrystallized bent bar. The presence of obstruction material or the existence of coarse grains or fragments cannot account for this lack of absorption, since the writers have found the same absence of absorption of the small grains by the reputedly "germinant" grains in both fine-grained brass and fine-grained tin when pieces containing a general strain gradient are annealed.

The conception that the formation of large grains is due to the existence of a germinant temperature corresponding to a given degree of strain would necessitate a discontinuity in grain size, a discontinuity separating normal grain growth from germination. No such discontinuity is observable, however. Furthermore, it is contended that the germinant temperature, which is said to give rise to larger grains, may be avoided by rapid heating through this temperature, and that a finer resultant grain size may be produced by the rapid heating, even though the annealing temperature is higher. If the grain sizes are to be compared, the heating rates must be substantially the same.

The detailed quantitative data presented here on recrystallization and grain growth in alpha brasses have shown clearly the complete absence of abnormality. Before attempting to apply to other metals the quantitative laws of grain growth of polycrystalline alpha brass it is necessary to consider in more exact terms the meaning of abnormal grain growth or germination. It is frequently contended that abnormal grain growth involves the formation of extremely large grains. Data have been presented that show that large grains may result from absolutely normal grain growth as represented by the low deformation portions of Fig. 1. *Therefore it appears best to consider abnormal grain growth as occurring if and when a coarser grain is produced at a given annealing temperature than is obtained by a higher annealing temperature, all other factors the same.* Among these factors those of greatest importance are: (1) original grain size, (2) temperature of deformation, (3) size of the section, (4) degree of deformation, (5) time of anneal, (6) the quantity of inert material that

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<sup>5</sup> H. M. Howe: *Trans. A.I.M.E.* (1916) 56, 582-599.

serves as an obstruction material, and (7) heating rate. When studying the effect of one of these variables, all the others must carefully be maintained constant.

While no attempt will be made to discuss each of these factors, it is well to point out that the increased grain size produced by slow heating as compared with rapid heating to the same temperature is a special study in itself and is not necessarily evidence of germination. Some metals are more sensitive to heating rate than others, depending upon the relative importance of the two factors, time and temperature, and the effect of the gradually increasing temperature upon the grain-growth process.

Any factor that raises the minimum temperature for grain growth, all other factors remaining the same, will result in coarser grains. Thus, if the degree of deformation is lowered, the temperature of deformation raised, the original grain size increased, or an obstruction material added, the grain size of the just recrystallized cold-worked material (no coalescence having taken place) is larger. Likewise, if the minimum temperature for grain growth by coalescence is increased by adding an obstruction material, the resulting grains are larger, though this growth is not abnormal because the time-temperature effects are not reversed. Thus, large grains produced in a steel containing an obstruction material, presumably aluminum oxide, have been attributed to "germination"<sup>6</sup>. The essential data are as follows: Heated at 1500° F., without  $\text{Al}_2\text{O}_3$  the grain size is moderately coarse, with  $\text{Al}_2\text{O}_3$  it is fine; heated at 1800° F., without  $\text{Al}_2\text{O}_3$  the grain size is coarse, with  $\text{Al}_2\text{O}_3$  it is extremely coarse.

These data represent the grain growth of austenite grains by coalescence. The two steels described behave normally because at 1500° F. the  $\text{Al}_2\text{O}_3$ -bearing steel has undergone little or no coalescence and is fine grained, while the other steel is slightly coarser at the same temperature because either coalescence has occurred to some slight extent or the absence of  $\text{Al}_2\text{O}_3$  has produced a slightly larger grain at the time of the alpha-gamma transformation. If the temperature were increased, say to 1600° F., the  $\text{Al}_2\text{O}_3$ -bearing steel might still show no grain growth while the other would show a slight increase in grain size. When the temperature is increased to 1800° F., however, the  $\text{Al}_2\text{O}_3$ -bearing steel is subjected to grain growth. The large grains are produced for reasons similar to those that cause the grains formed by the recrystallization of a cold-worked metal reduced 3 per cent before annealing to be coarser than if the same metal were reduced 15 per cent and recrystallized. The latter relationship is represented by Fig. 1. Therefore the large grains produced in the  $\text{Al}_2\text{O}_3$ -bearing steel would be still larger if it were heated to a higher temperature; say, 1900° F. Hence 1800° F. is not the "critical temperature" and that particular  $\text{Al}_2\text{O}_3$  content is not the "critical

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<sup>6</sup> E. C. Bain: *Trans. Amer. Soc. Steel Treat.* (1932) 20, 385-428.



degree of obstruction" for "germination"; for if it were, the steel would be finer grained when heated to 1900° F. than it is when heated to 1800° F.

Referring again to the reputedly abnormal grain growth produced by Sauveur and by Chappell<sup>7</sup> in mild steel by annealing after various types of cold deformation, the coarse grains produced in the areas of low deformation are called "germinant grains." The magnification of the photographs taken by Sauveur and by Chappell are only 5 or 6 diameters and the grains are unusually large; even the grains that have undergone no grain growth (i.e., that part of the specimen having little or no strain) are rather large, but the difference in grain size from the coarsest to the finest is no greater than that obtained in the alpha-brass general strain-gradient specimens that were found to have normal growth for all conditions of time, temperature, and degree of strain. Indeed, qualitatively the grain sizes produced by Sauveur and by Chappell in steel containing various degrees of strain are very similar to those found by the writers when studying the recrystallization of brass. The greater grain size (but not greater grain-size difference) found in the low-carbon steel is an attribute of the metal rather than of the recrystallization process, perhaps just as brass is generally finer grained than copper, or as Monel metal is finer grained than tin or aluminum.

Jeffries<sup>8</sup> cites the data obtained by Ruder<sup>9</sup> on recrystallization of silicon sheet steel as evidence of a finer grain produced by rapid heating through the "germinant temperature." Ruder's photographs clearly show that the steel deformed 5 per cent is coarser when annealed at 800° C. than when annealed at 750° C., though the latter temperature was claimed to be the "germinant temperature." It is true, however, that when the 2.5 per cent deformed piece is heated to 950° C., it is finer than when heated to 850° C. This refinement might be due, however, not to rapid heating through the "germinant temperature" of 850° C., but to the gamma-alpha transformation, unless the silicon were high enough to destroy the A<sub>3</sub> transformation. The possibility of abnormal grain growth in silicon sheet steel is being investigated by the writers.

Aluminum is a metal that is prone to contain large grains. The recrystallization of this metal has been studied very superficially by many and in considerable detail by E. Wetzel<sup>10</sup>, H. Hanemann and R. Vogel<sup>11</sup>, and H. Rohrig<sup>12</sup>.

The work of E. Wetzel is particularly interesting. When studying originally fine-grained material, this investigator found the grain growth

<sup>7</sup> Z. Jeffries and R. S. Archer: The Science of Metals, 1924.

<sup>8</sup> Z. Jeffries: Reference of footnote 7.

<sup>9</sup> W. E. Ruder: Discussion of reference of footnote 5.

<sup>10</sup> E. Wetzel: *Mitteilungen a. d. Kaiser Wilhelm Inst. f. Metallforschung* (1922) 1, 24.

<sup>11</sup> H. Hanemann and R. Vogel: *Hausztisch. V. A.W.* (1923)

<sup>12</sup> R. Rohrig: *Ztsch. f. Metallkunde* (1924) 16, 265.

to be normal; i.e., analogous to that illustrated by the data presented here on alpha brass. Enormously large grains were obtained when aluminum containing low degrees of cold deformation (requiring a high crystallization temperature) was recrystallized. However, in every instance the recrystallized grains increased in size with increasing temperature, showing the absence of critical conditions required for germination. But when this investigator studied specimens having large grains initially, he decided that the results lacked uniformity. Careful study of his photographs shows that he was unable to recognize recrystallized and unrecrystallized material when the grain sizes before and after were approximately the same, thus producing no contrast. No hardness data were taken to aid in this differentiation. However, his photographs clearly show that when the original grain size is increased, the effect is similar to a reduced degree of cold-work. No abnormality or germination was produced by this investigator although he used a wide variety of temperatures, degrees of deformation, and original grain sizes.

Hanemann and Vogel present very interesting data on grain sizes produced under various types of hot-work. Their work shows that the relation of the degree of deformation and temperature to the grain size produced by hot-work is very similar qualitatively to that produced by cold-work and annealing, provided that the rate of deformation is rapid. Their work also shows that when the deformation is accomplished below the hot-working temperature the increasing temperature of cold-work has the effect on grain size similar to the addition of an obstruction material or a lesser degree of reduction.

While large grains (several centimeters in diameter) were produced in aluminum and its alloys by all these investigations, there was not a single instance of abnormal grain growth; i.e., production of a coarser grain growth at a given annealing temperature than that produced by a higher annealing temperature. Indeed, the only instances of such behavior have occurred in cold-drawn tungsten wire, and perhaps in molybdenum. It should be pointed out that the cases of most exaggerated grain growth by germination in tungsten occur in small sections where the limited dimensions cause a preferential growth of a relatively few nuclei of such orientation that it permits growth parallel to the axis of the wire.

In the work reported here, all degrees of deformation were heated for a wide variety of temperatures and times, each piece being placed in a furnace already at the desired annealing temperature. In not a single instance did rapid heating to a higher temperature produce a finer grain size for a given percentage of reduction. On the basis of this evidence and the numerous published data on other metals, the writers conclude that rapid heating to a higher temperature will not cause a given piece of cold-worked metal, excepting tungsten and perhaps molybdenum, to be recrystallized to a grain size finer than that obtained by recrystallizing at



- a* and *b*. Reduced 36 per cent and heated  
*(a)* 5 min. at 600° C., *(b)* 15 min. at  
450° C.  
*c* and *d*. Reduced 17 per cent and heated  
*(c)* 15 min. at 600° C., *(d)* 2700 min. at  
450° C.  
*e*. Reduced 20 per cent and heated 5 min.  
at 600° C.

FIG. 2.—MICROSTRUCTURE OF SAMPLES OF 66-34 BRASS, REDUCED IN AREA BY DRAWING AND RECRYSTALLIZED.  $\times 75$ .

a lower temperature, all other factors being the same. Indeed, the higher temperature will always give a coarser grain, because of coalescence. It is evident that this so-called germinant temperature is merely the minimum temperature for a given time of anneal at which the metal will recrystallize. When the percentage of deformation is low, the resultant new grains are large. Furthermore, the grain size in alpha brass produced when recrystallization is just complete for a given deformation is the same whether it is the result of annealing for a short time

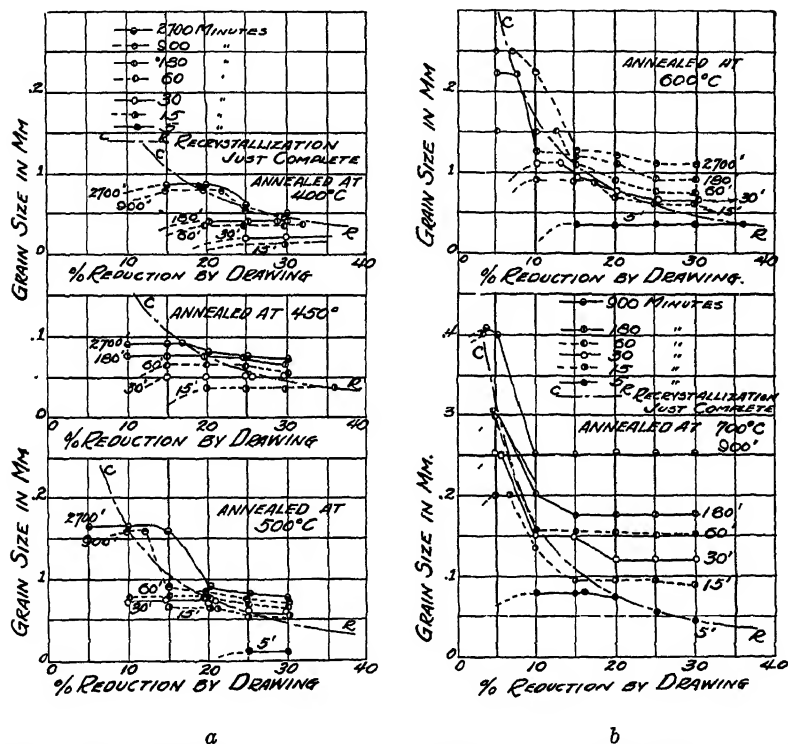


FIG. 3.—RELATIONSHIP OF GRAIN SIZE TO PERCENTAGE OF DEFORMATION BY COLD-DRAWING AFTER VARIOUS TEMPERATURES AND TIMES OF ANNEAL.

at a high temperature or for a long time at a low temperature. In Fig. 2, *a* and *b* are samples of 66-34 brass reduced 36 per cent in area and recrystallized, the former by heating 5 min. at 600° C., and the latter by annealing 15 min. at 450° C. No coalescence occurred in either instance. Figs. 2c and 2d show the same brass reduced 17 per cent in area by cold-drawing and recrystallized without coalescence, the first having been annealed 15 min. at 600° C. and the second 2700 min. at 450° C.

Fig. 3 shows the relationship of grain size to percentage of deformation by cold-drawing after various temperatures and times of anneal. The superimposed curve *CR* (from Fig. 1a) clearly shows the grain size just at

complete recrystallization with no coalescence. The grain sizes to the right and above the line *CR* have grown by coalescence; those to the left and below this line occur in regions that have not yet reached complete recrystallization. The grain sizes to the right of the line *CR* decrease with increasing degree of deformation, and the greatest amount of coalescence, as measured by the vertical distance from the grain-size curve to the curve *CR*, occurs at the maximum degree of deformation where the grains originally were finest at the time when the metal had just recrystallized.

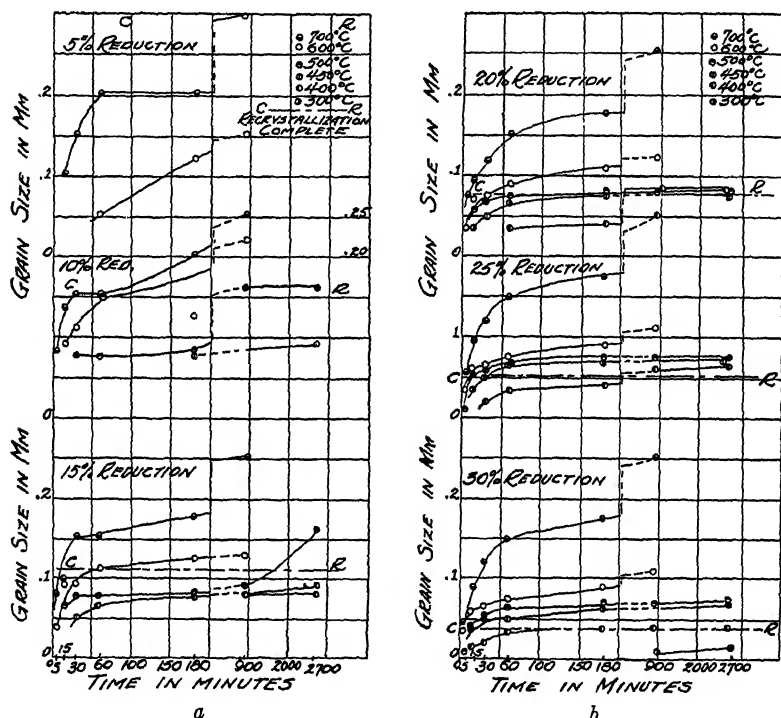


FIG. 4.—GRAIN SIZE-TIME CURVES AT VARIOUS PERCENTAGES OF DEFORMATION AT CONSTANT TEMPERATURE FOR COLD-DRAWN BRASS.

tallized. Minimum coalescence occurs in the regions of lower deformation and is zero at the line *CR*. The left end of the grain-size curves represents the minimum percentage of deformation at which new grains could be observed at high magnification. Except for these most distant grains, which were last to appear, the new grains in the partly recrystallized portions of the bar are alike in size and also are equal in size to those where recrystallization is just complete. This is represented by the horizontal portions of the grain-size-deformation curves to the left of the line *CR*. It follows that the rate of growth of the new grains is independent of the degree of deformation.

If the grains that have the same size in the partially recrystallized areas also have the same rate of growth at various degrees of strain, they must also have started to form at essentially the same time. This is illustrated by specimens 7 and 8 of Table 1; the former, heated at 600° C. for 5 min., showed new grains from 36 per cent to 12 per cent reduction, and the latter, maintained at 600° C. for 15 min., showed new grains back only to 6.5 per cent reduction. It is reasonable to suppose, therefore, that the new grains at 20 per cent and 36 per cent deformation

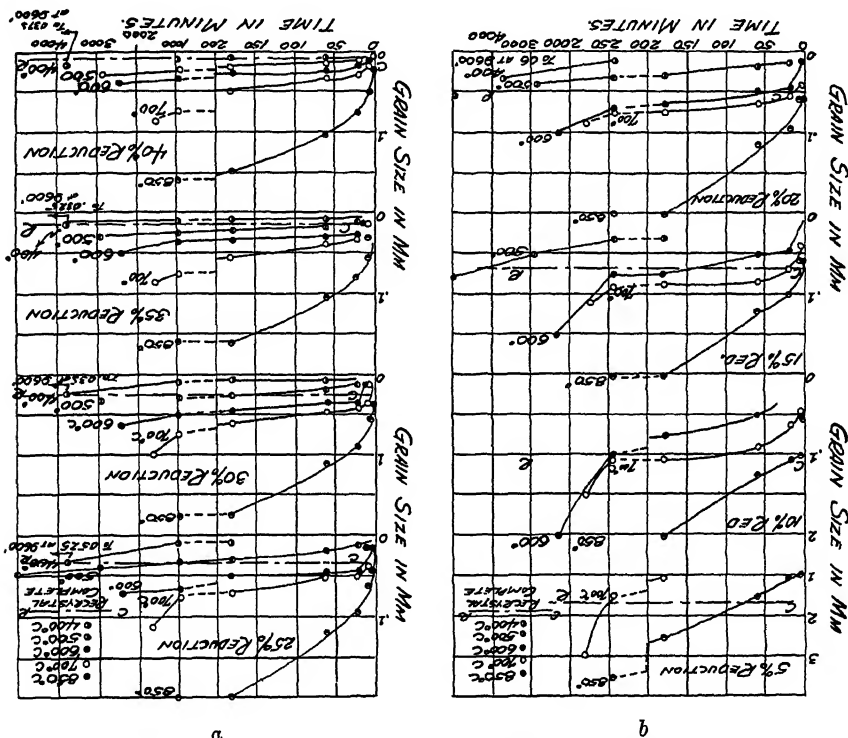


FIG. 5.—GRAIN SIZE-TIME CURVES AT VARIOUS PERCENTAGES OF DEFORMATION AT CONSTANT TEMPERATURE FOR COLD-ROLLED BRASS.

made their appearance about the same time. That the new grains are the same size is illustrated by Figs. 2a and 2e, which show the alpha brass after being heated 5 min. at 600° C. with a previous reduction by drawing of 36 and 20 per cent, respectively. That the rate of grain growth in partially recrystallized bars is independent of the degree of deformation is further substantiated by the similarity of the slopes of the grain size-time curves of Figs. 4 and 5 at the various percentages of deformation but at constant temperature. Thus a comparison between the rates of growth at 700° C. by recrystallization of brass at 30 per cent reduction by rolling and at 20 per cent shows the former to be completely recrystallized at

0.025 mm. and the latter at 0.05 mm. (Fig. 5). The slopes of the grain size-time curves for the 30 per cent and 20 per cent reductions are similar up to 0.025 mm. When the degree of deformation is markedly different, the new grains in the areas of low deformation are smaller because they begin to grow at a later time.

Fig. 4 shows the relationship of grain size to time, in minutes, for cold-drawn brass. Because of the great difference in time, it was necessary to break and to increase the time scale at 200 min. The curves for

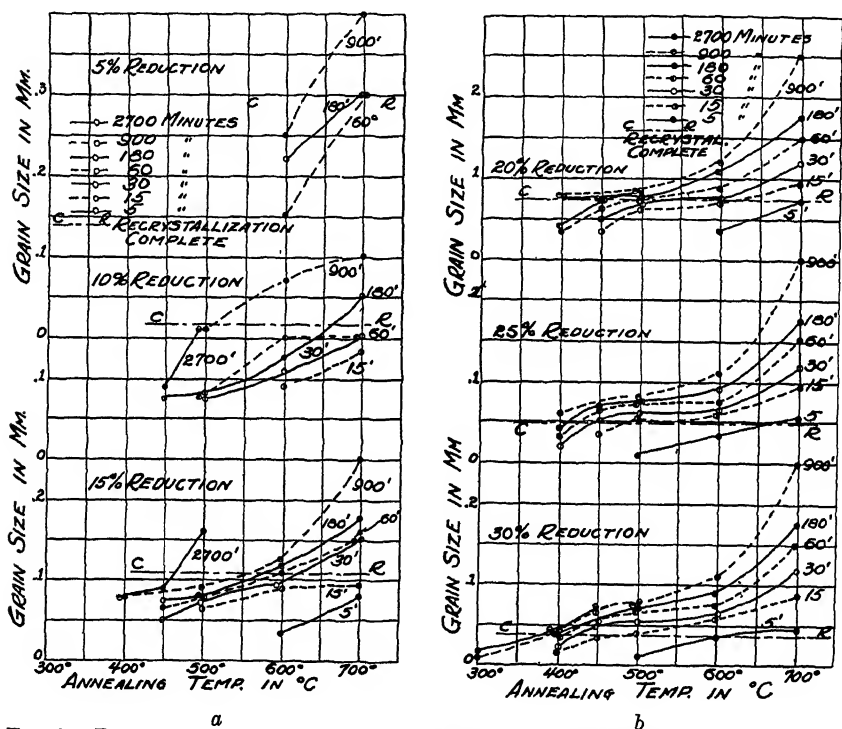


FIG. 6.—RELATIONSHIP OF GRAIN SIZE TO TEMPERATURE OF ANNEAL FOR COLD-DRAWN ALPHA BRASS, AT FIXED ANNEALING PERIODS.

the same deformation but of different annealing times are grouped together. Since the grain size just after complete recrystallization is independent of time and temperature, it may be represented as a constant value by the line *CR*. The grain-size curves above this line represent coalescence; those below represent the size of grains in partially recrystallized areas. It will be observed that the increase in grain size with time is similar whether the new grains grow at the expense of deformed material (recrystallization) or at the expense of equiaxed unstrained grains (coalescence). Fig. 5 shows similar relationships of grain size to annealing time for cold-rolled brass.

Fig. 6 shows the relationship of grain size to temperature of anneal at various fixed annealing periods for cold-drawn alpha brass. As before, the grain size just after complete recrystallization is constant for a given degree of deformation, the horizontal line *CR* representing the value as taken from Fig. 1*a*. There is no flexure in these curves where recrystallization is complete, a condition that shows that the effects of temperature at constant time and degree of deformation are similar, whether the new grains are growing at the expense of strained material (recrystallization) or the growing grains are absorbing unstrained new grains (coalescence). Incidentally, the intersection of the curve *CR* with the grain size-temperature curves gives the recrystallization temperature at the various annealing times for a given degree of deformation; its accuracy is dependent upon the accuracy of the data.

#### EFFECT OF TEMPERATURE GRADIENT

Four bars of coarse-grained alpha brass, having been reduced by cold-rolling 5, 15, 30 and 45 per cent, respectively, were heated locally to 700° C. and the ends were cooled in water so that the temperature dropped from 700° to about 75° C. in 12 cm. on one end, and from 700° to about 90° C. in 4 cm. at the other end. Thus two different temperature gradients were produced for each of the four bars. The steeper gradient was about 150° C. per centimeter. These gradients were maintained uniformly for 24 hr. before the bars were examined for grain size. In each of the four bars there was no evidence of abnormal grain growth, a fact that does not agree with the abnormal grain growth produced by a temperature gradient as postulated by the theory presented by Jeffries<sup>13</sup>. At the cold end, in each instance, there was a region just completely recrystallized, and from this completely recrystallized region toward the cold end there was an area partially recrystallized, the quantity of new grains decreasing from 100 per cent at the region just completely recrystallized to zero where the temperature had been just too low to allow the formation of new grains. The grains at the point of just complete recrystallization were the size characteristic of this material when recrystallized without coalescence for the given degrees of deformation. These grain sizes are marked on Fig. 1*a* by the four points *a*, one for each of the four degrees of deformation. The grain sizes at the two ends of each bar where recrystallization was just complete were identical. The size of the grains from the point of just complete recrystallization to the maximum degree of heat increases because of coalescence. Thus, it is important to observe that the temperature gradient produces grain growth without any abnormalities at the regions where recrystallization is barely possible; i.e., at the regions where recrystallization is just complete.

<sup>13</sup> Z. Jeffries: *Trans. A.I.M.E.* (1916) **56**, 571-581.



The impossibility of abnormal grain growth here is due to two conditions: (1) As at the similar regions of the bars given a strain gradient, the grains at the region of just complete recrystallization are bordered on the one side by unstrained grains of essentially the same size as those in the region just completely recrystallized, and on the other side by metal that is almost completely recrystallized. The size of the new, unstrained grains of the latter portion is essentially the same as that of the grains at the region where recrystallization is just complete. (2) The low temperature does not favor mobility of the atoms of the metal and, therefore, is unfavorable to the growth of large grains.

Since there remained the possibility that abnormal grain sizes might result from a combination of (1) production of a still steeper temperature gradient, (2) a fine-grained material to begin with, and (3) the production of a strain gradient that would augment the effect of the temperature gradient, an experiment along these lines was conducted by the writers. However, there was no evidence of abnormal grain growth produced by this favorable combination of conditions.

#### EFFECT OF PREVIOUS LOW-TEMPERATURE ANNEALS

In order to investigate the effect of low-temperature anneals on the number of nuclei and hence on the grain sizes just after complete recrystallization, pieces of coarse-grained alpha brass were uniformly strained by reducing the thickness 5, 15, 30 and 50 per cent by rolling. Sets of pieces were annealed 24 hr. at 190°, 225° and 275° C., respectively. The pieces that had been reduced 50 and 30 per cent increased 1.6 and 0.7 in Rockwell E hardness when annealed 24 hr. at 190° C. Similar pieces showed partial recrystallization when annealed at 225° C., and the piece having the 50 per cent reduction was completely recrystallized when annealed at 275° C. for 24 hr. The two pieces having the lowest reductions decreased in hardness with all three anneals. All the pieces, including specimens of each reduction without a previous anneal, were then given a 20-min. anneal at 500° C. The specimens having a 5 per cent reduction did not form new grains, the pieces having a 15 per cent reduction were partially recrystallized, while the pieces having 30 and 50 per cent reductions were, of course, completely recrystallized. Regardless of the temperature of the preliminary anneal, the grain sizes after the second anneal were the same as those produced in the corresponding pieces without any previous low-temperature anneal. Very little or no coalescence occurred in any instance; hence the resulting grain size is indicative of the number of nuclei that grew to form new grains.

#### CONCLUSIONS

On the basis of the data obtained by the writers on alpha brasses and of a critical examination of the data obtained by other investigators on

other metals, the following summary of the principal features of grain growth is presented:

1. On the basis of rather vague existing usage of the term and for the purpose of exactness, abnormal grain growth or germination has been defined here as consisting of the formation of larger grains by annealing a cold-worked material than can be obtained by annealing the same metal at some higher temperature, all other factors being the same.
2. Abnormal grain growth is extremely rare, for no evidence of such a phenomenon is furnished by the published accounts of this subject, except in tungsten and perhaps molybdenum.
3. Normal grain growth can account for nearly all if not all instances of large grains or extremely large grains that may occur in aluminum, brass, steel (such as that used by Sauveur and by Chappell when producing their examples of so-called "germination"), iron, etc.
4. The "laws" and principal concepts of "normal grain growth" or simply "grain growth" are:
  - a. Grains may grow at the expense of cold-worked grains (recrystallization) or at the expense of unstrained grains (coalescence).
  - b. The grain size just after complete recrystallization, in alpha brass at least, is independent of time and temperature and dependent only upon the composition and history of the material prior to the deformation, and upon the degree of deformation.
  - c. Annealed cold-worked metals are coarser with higher annealing temperatures, since rapid heating to a higher temperature through the so-called "germinant temperature" produces a coarser rather than a finer grain.
  - d. Coarser grains in the just recrystallized metal are produced by increasing the recrystallization temperature by the following:
    - (1) A decrease in the degree of cold deformation.
    - (2) The addition of an obstruction material, particularly when the degree of reduction is low.
    - (3) An increase in deformation temperature.
    - (4) An increase in original grain size.
  - e. An obstruction material when present in an annealed material raises the minimum temperature of coalescence, with the consequent formation of larger grains than are produced in a similar metal at the same temperature without the obstruction material. This is analogous to the four causes (listed above) of greater grain size produced during grain growth by recrystallization.
  - f. Coarse grains are not necessarily indicative of germination, because very coarse grains (several centimeters in diameter) can be produced by the methods listed above and at the same time conform with the rules of normal grain growth.

- g.* The region of coarse grains that frequently are called "germinant grains" produced by "abnormal" grain growth occurs always at low deformations and occupies the area where grain growth is barely possible; i.e., the region of minimum deformation at which new grains can form. This is frequently called the "critical" or "germinant" degree of strain. Such large grains, however, are formed in conformity with the laws of normal grain growth.
- h.* The rate of growth of new grains in partially recrystallized alpha brass is independent of the degree of strain.
- i.* The grain size increases with time and temperature, the increase obeying the same laws whether the growth be at the expense of cold-worked metal (recrystallization) or at the expense of some of the newly formed, unstrained grains (coalescence).
- j.* The number of nuclei that serve as centers of recrystallization in alpha brass is independent of temperature, or very nearly so, and is not affected by a previous low-temperature anneal.
- k.* Temperature gradients in alpha brass do not give rise to any grain-growth abnormalities.
- l.* Decreased rate of heating and small section size, for at least some cold-worked metals, increase the grain size markedly during annealing.

## Aluminum-copper-nickel Alloys of High Tensile Strength Subject to Heat-treatment

BY W. A. MUDGE\* AND PAUL D. MERICA,† MEMBER A.I.M.E.

(New York Meeting, February, 1935)

ONE of the most prominent features of our present-day industrial development is the ever-increasing demand put upon materials of construction. Engineering ingenuity, within the past 25 years, has been unusually active, and in some fields at least engineers frankly say that engineering design has progressed as far as the limitations imposed by the properties of the present materials of construction will permit. Consequently, they are today demanding improvement in their working materials and seeking new ones, through the aid of which the present limitations of design may be overcome.

The activity of this search is evident in all fields, but it is particularly so in that of structural materials required to be resistant to corrosion. The corrosion resistance of metals and alloys is never absolute and all-inclusive; a particular alloy will withstand some corrosive conditions well and fail utterly under others. Furthermore, other properties, physical and mechanical, required in conjunction with corrosion resistance vary considerably for different commercial applications. One wants a soft, ductile sheet metal resistant to atmospheric corrosion; another, a high-strength alloy resistant to sulfuric acid.

The last decade has witnessed active and definite progress in the development of high-strength, corrosion-resisting alloys. In June, 1924, a symposium by the American Society for Testing Materials, on Corrosion-resistant, Heat-resistant and Electrical-resistance Alloys, disclosed no less than 60 commercial alloys the properties of which were described as being suitable for industrial service where corrosion resistance was a feature. Today the number of these alloys has been doubled, at least.

In addition, economy in design and construction through decreased weight has given considerable impetus to the improvement of alloys of which the mechanical properties may be improved by heat-treatment.

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\* Metallurgist, Huntington Works, The International Nickel Co., Inc., Huntington, W. Va.

† Assistant to the President, The International Nickel Co., Inc., New York.

The alloys generally described as the age-hardening alloys<sup>1\*</sup> have been intensely studied and many of them developed to a sound commercial basis. Finally, the metallurgist has definitely entered the era of rational alloy building.

This paper describes a new alloy series within the corrosion-resistant category, certain compositions of which have a considerable resistance to corrosion toward most media and which, in addition, can be made to assume a wide range of useful mechanical properties through proper heat treatment. This alloy series is composed of aluminum, copper and nickel, the proportions of which may vary considerably (i.e., aluminum, 3 to 5 per cent; nickel, 40 to 90 per cent; copper, balance) without altering the susceptibility to heat-treatment, although with some variations in corrosion resistance and of mechanical properties. Thus, the properties and behavior of one typical composition within this range serves to illustrate those of the whole group of alloys. Such a composition is: carbon, 0.15 per cent; sulfur, 0.005; manganese, 0.50; silicon, 0.25; iron, 1.50; aluminum, 4.00; copper, 28.00; nickel, balance. The discussion to follow will relate principally to this composition.

This alloy is obtained simply by adding 4 per cent of aluminum to ordinary Monel Metal;<sup>†</sup> and it was, indeed, this composition that was first studied and of which the interesting properties discovered are to be described. Later it was found that the copper-nickel ratio could be varied considerably without undue effect upon the properties, provided the aluminum content was kept at the amount indicated above.

Aluminum-Monel Metal,<sup>‡</sup> as it will henceforth be called, for convenience, was discovered in 1919 by one of the authors<sup>2</sup>. Later study by the other author developed the fact that its properties could be altered considerably by heat-treatment<sup>3</sup>. Independently, it was discovered later, Leon Cammen<sup>4</sup> had made a similar alloy and had noted its remarkable hardness and tensile properties, but had not observed that it was affected by heat-treatment. In 1928, U. S. Patent No. 1675264 was issued to T. S. Fuller, in which an optimum ratio of carbon to aluminum was claimed. The authors have been unable to find any other description of alloys of this type in the literature.

In England the properties of copper-rich alloys, containing up to 10 per cent of both nickel and aluminum have been studied in detail by Read and Greaves<sup>5</sup>. Several investigations have been made of the aluminum-rich alloys with copper and nickel, and Austin and Murphy<sup>6</sup> have made a systematic and most valuable study of the equilibrium in

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\* References are at the end of the paper.

† The name "Monel Metal" is a registered trade-mark.

‡ For convenience, the term Monel Metal will be used herein to describe a nickel-copper alloy containing about 68 per cent nickel.

the ternary system aluminum-copper-nickel, without, however, making any comment on the physical properties of the ductile alloys of this system. Jones, Pfeil and Griffiths<sup>7</sup> and Brownsdon, Cook and Miller<sup>8</sup> have investigated the copper-rich aluminum-copper-nickel alloys and described the results obtained by heat-treatment.

## HEAT-TREATMENT AND MECHANICAL PROPERTIES OF ALUMINUM-MONEL METAL

The response of this alloy to heat-treatment is somewhat similar to that of duralumin and to that of the nickel-aluminum bronzes described

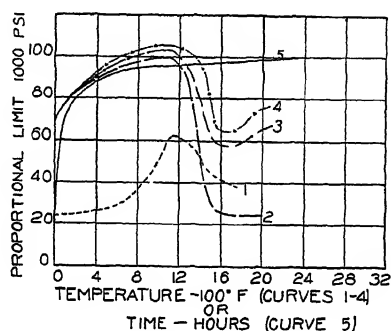


FIG. 1.—EFFECT OF HEAT-TREATMENT UPON MECHANICAL PROPERTIES (PROPORTIONAL LIMIT IN TENSION) OF ALUMINUM-MONEL METAL. ALL TESTS MADE WITH STANDARD 0.505-IN. SPECIMENS.

CURVE 1. Abscissas: Temperatures from 0 to 3200° F. Hot-rolled and oil-quenched from 1500° F. followed by a draw for 1 hr. at the temperatures shown, followed by air cooling.

CURVE 2. Abscissas: Temperatures from 0 to 3200° F. Cold-drawn, followed by heating for 1 hr. at the temperatures shown and quenching in oil.

CURVE 3. Abscissas: Temperatures from 0 to 3200° F. Cold-drawn, followed by heating for 1 hr. at the temperatures shown and cooling in air (in form of 0.505-in. test specimens).

CURVE 4. Abscissas: Temperatures from 0 to 3200° F. Cold-drawn, heated 1 hr. at the temperatures shown, oil-quenched and drawn 12 hr. at 1100° F., cooled in air.

CURVE 5. Abscissas: drawing period from 0 to 32 hours. Hot-rolled, oil-quenched from 1500° F. and drawn for the periods shown at 1100° F. Cooled in air.

by Read and Greaves<sup>5</sup> and different from that of steel. It is almost the reverse of that for steel, since the alloy is soft when quenched and hard when slowly cooled. It is similar to duralumin in these respects, but duralumin cannot be slowly cooled to its full hard condition as can Aluminum-Monel Metal.

Figs. 1 and 2 illustrate the effect of heat-treatment upon the properties of this alloy. Fig. 2 shows the relation of the several mechanical properties to Brinell hardness. This curve has been made as result of tests on many different melts of the alloys and will be found useful for reference

TABLE 1.—*Properties of a Hot-rolled Carbon-free Aluminum-Monel Metal Alloy Containing 4.66 Per Cent Aluminum*

Heat Treatment	Proportional Limit, Lb. per Sq. In.	Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Reduction of Area, Per Cent
Quenched in water after 1 hr. at 1500° F. ....	22,000	30,000	84,000	44	67
Quenched in water after 1 hr. at 1500° F., followed by 1 hr. at 1100° F. and air cooling....	47,500	57,500	106,250	34	45
Quenched in water after 1 hr. at 1500° F., followed by 7 hr. at 1100° F. and air cooling..	56,250	67,000	115,000	15	19

TABLE 2.—*Effect of Heat-treatment on Aluminum-copper-nickel Alloy Containing 0.07 Per Cent Carbon, 3.78 Per Cent Aluminum, 51.70 Per Cent Copper, and 43.17 Per Cent Nickel*

Heat Treatment	Proportional Limit, Lb. per Sq. In.	Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Reduction of Area, Per Cent
Quenched in water after 1 hr. at 1800° F. ....	18,500	39,500	86,500	51	56
Quenched in water after 1 hr. at 1500° F. ....	20,500	45,950	90,750	48	61
Quenched in water from 1500° F., heated 7 hr. at 1100° F. and quenched.....	88,500	112,600	149,000	25	37
Quenched in water from 1500° F., heated 7 hr. at 1100° F. and slowly cooled.....	90,000	114,650	152,200	24	38

TABLE 3.—*Effect of Chemical Composition upon Heat-treatment of Aluminum-copper-nickel Alloys*

Composition, Per Cent			Proportional Limit, Lb. per Sq. In.	
Al	Cu	Ni	Minimum as Quenched	Maximum as Quenched and Drawn
4.42	4.34	89.54	17,000	47,000
4.11	9.30	85.53	21,500	75,000
4.00	25.82	65.83	25,000	100,000
3.78	51.70	43.17	20,500	90,000

alloys "age." At elevated temperatures the rate of aging increases with temperature until, at 1100° F., a maximum is reached which is taken as the optimum hardening temperature. Table 4 gives data to illustrate this effect.

TABLE 4.—*Aging of Aluminum-Monel Metal*

No.	Heat Treatment	Proportional Limit, Lb. per Sq. In.	Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Reduction of Area, Per Cent
1	Sample tested immediately after quenching from 1500° F.	27,000	39,250	95,000	48	67
2	Same after 6 weeks at 75° F...	31,000	41,500	97,000	50	61
3	No. 1 after 2 weeks at 450° F..	30,000	40,500	98,500	49	67
4	No. 1 after 18 months at 450° F. ....	60,500	80,250	121,000	43	53
5	No. 1 after 2 weeks at 650° F..	50,250	67,250	110,750	44	55
6	No. 1 after 18 months at 650° F. ....	81,500	96,500	137,750	32	40
7	No. 1 after 2 weeks at 800° F..	83,500	102,000	147,500	28	40
8	No. 1 after 2 months at 800° F.	93,000	114,000	157,000	23	35
9	No. 1 after 24 hours at 1100° F.	100,000	119,000	162,000	20	30
10	Quenched from 1500° F., drawn 1 hr. at 1100° F., quenched, and tested immediately.....	60,000	78,000	122,000	40	50
11	Same after 6 weeks at 75° F..	71,000	85,000	138,000	39	52

The alloys cannot be over-aged. If the alloys, after aging or hardening at 1100° F., are heated above 1100° F. and rapidly cooled, which will result in some softening, and then rehardened at 1100° F., their hardness is practically restored to its original maximum value. This demonstrates a re-solution of the submicroscopic hardening particles in the parent lattice, and not overgrowth; or perhaps alternatively demonstrates a reversal of the transformation upon cooling with re-formation of the solid solution stable at the higher temperatures.

#### *Tensile Properties at Higher Temperatures*

Aluminum-Monel Metal, if previously in the fully heat-treated or hard condition, may be heated to 1075° to 1100° F. and held apparently for any reasonable length of time and after either rapid or slow cooling will still retain its full hardness and strength. It also actually retains its properties remarkably well at higher temperatures, as Table 5 shows. Equipment was not available for an accurate determination of the proportional limit at the elevated temperatures, therefore these values are not reported. The proportional limit at 800° F. was judged to be



approximately 90,000 lb. per sq. in., and was so high in comparison with that shown in tests of other alloys, and even of alloy steels, that the following experiment was carried out to determine whether this value represented a relatively proportional limit or whether slow yielding would occur. A 0.505 in. specimen having, at 75° F., a proportional limit of 100,000 lb. per sq. in. was held for 5 hr. in a testing machine at 800° F. with the beam balanced at 90,000 lb. per sq. in. No signs of flow of the specimen under the load were noticed during the test.

### CHEMICAL AND OTHER PROPERTIES

The corrosion resistance of Aluminum-Monel Metal, in both the soft and fully hard conditions, appears to be similar in all respects to that of Monel Metal itself, the corrosion-resisting properties of which are elsewhere described in detail. Actual tests, indeed, in acids and in salt spray, have shown it to possess somewhat superior resistance to corrosion.

The presence of the aluminum renders the alloy nonmagnetic down to at least  $-110^{\circ}$  F.<sup>10</sup> and decreases the density by about 5 per cent.

### MECHANICAL WORKING OF THE ALLOYS

This group of alloys can be hot-rolled and cold-rolled and hot-forged, although hot working must be carried out within definite temperature limits; viz., 2100° to 1700° F. The alloys are less malleable through the temperature range 1500° to 900° F. and cannot be worked satisfactorily through that range. It is very significant that this is also the temperature range within which the transformations occur that are responsible for the hardening effect.

Cold rolling is of course more difficult than with ordinary Monel Metal, since the alloys are harder and stiffer, yet with sufficient power it can be done. Naturally, it is preferable to use the soft (quenched) alloy for any cold-working operation. An alloy, having initially the properties shown in Table 6, is hardened in the usual manner by cold work and may be hardened further by heat-treatment.

Cold drawing of wire for spring uses is likewise more difficult than with ordinary Monel Metal, but with soap lubricants and a 50 per cent increase of power the operation can be carried out successfully. The ability of the alloys to be heat-treated and thereby hardened beyond their cold-worked hardness makes it possible to obtain unusually high-strength spring material for corrosion-resisting alloys. Table 7 shows the tensile properties obtained with several sizes of wire as a result of heat-treatment following a 75 per cent cold reduction from an originally soft (quenched) condition. After cold drawing and before hardening the breaking strengths were 173,600 lb. per sq. in. for the 4.00 per cent Al alloy and 159,000 lb. per sq. in. for the 3.75 per cent Al alloy.

*Machining*

Aluminum-Monel Metal can be machined in all tempers up to 300 Brinell by the methods recommended for Monel Metal; i.e., including the use of high-speed steel tools with somewhat sharper angles and greater clearances than are usual for steel. Whereas, however, the alloy can be machined practically as easily as Monel Metal, as long as its Brinell hardness is not greater than 250 it requires more power to machine in the higher stages of hardening, and subjects the tool to greater wear. With a Brinell hardness of 250 to 275 it can still be machined readily. In the full hard condition, with a Brinell hardness greater than 300,

TABLE 5.—*Effect of Temperature on Tensile Properties\**

Tested at	Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Reduction of Area, Per Cent
75° F.	121,000	161,000	20	34
600° F.	118,600	157,600	18	31
800° F.	116,500	135,200	18	28
1000° F.	102,800	124,600	9	10

\* In usual short-period test.

TABLE 6.—*Strength and Hardness of Cold-rolled 0.043-in. Strip*

Properties	Soft (as quenched)	Cold-rolled 0.086 to 0.043 In.	Cold-rolled 50 Per Cent and Hardened
Yield point, lb. per sq. in. ....	43,700	75,000	100,000
Tensile strength, lb. per sq. in. ....	91,800	139,000	145,000
Elongation, per cent in 2 in. ....	41	11	2.5
Shore hardness (Universal).....	21	50	55
Erichsen ductility (cup depth, in., with 7/8-in. dia. ball and 1 1/8-in. dia. ring)..	0.600	0.300	0.100

TABLE 7.—*Tensile Properties of Spring Wire*

Diameter, In.	Al, Per Cent	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Reduction of Area, Per Cent
0.080	4.00	210,900	2	21*
0.100	4.00	210,000	3	28
0.140	3.75	201,000	3	20
0.160	3.75	200,000	3	18
0.200	3.75	210,200	3	18
0.250	3.75	200,000	5	20

\* Each wire could be coiled around its own diameter without fracture.

it is not machinable. Fortunately, there exists the option of quenching soft for machining and drawing back at about 1100° F. subsequently to

develop the optimum mechanical properties. Details for machining may be found in a special technical bulletin published by The International Nickel Company, Inc.

### MANUFACTURE AND USES OF THE ALLOYS

Aluminum-Monel Metal offers some difficulties in manufacture, which have been mainly responsible for the slowness of its commercial development. Today it can be secured in most of the commercial hot-worked and cold-worked sizes. In order to facilitate heat-treatment in the field, all hot-worked products are suitably quenched after hot rolling or forging. Table 8 gives tentative specifications for the alloys in different tempers.

Although it is dangerous to attempt to prophesy definite possible uses for new materials, the general field of usefulness of the aluminum-copper-nickel alloys can be indicated. The features of Aluminum-Monel Metal, and indeed of the whole series, are the very high tensile strength and hardness that can be developed by heat-treatment; mechanical properties that are comparable with those of a heat-treated alloy steel *but in conjunction with substantial resistance to corrosion*. Wherever, therefore, a substantial degree of corrosion resistance is required in conjunction with such high physical properties, particularly at elevated temperatures, these alloys should be of value. Turbine blading, pump rods and steam-valve trim, corrosion-resistant springs and cutlery would appear to be ideal fields for these alloys.

TABLE 8.—*Tentative Specification of Aluminum-Monel Metal*

Hardness Grade	Proportional Limit, Lb. per Sq. In.	Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Reduction of Area, Per Cent	Brinell Hardness Number, 3000 Kg.
A	60,000 max.	80,000 max.	120,000 max.	40 min.	50 min.	225 max.
B	60-80,000	80-100,000	120-140,000	30 min.	35 min.	225-275
C	80-100,000	100-120,000	140-160,000	20 min.	25 min.	275-325
D	100,000 min.	120,000 min.	160,000 min.	15 min.	20 min.	325 min.

### SUMMARY

A new series of corrosion-resistant alloys is described, having a wide range of mechanical properties developed through proper heat-treatment. These alloys are of the aluminum-copper-nickel type, containing preferably: 3 to 5 per cent Al, 40 to 90 per cent Ni, balance, Cu. Of these a typical alloy is that produced by the addition of 4 per cent of aluminum to Monel Metal, and this paper describes, as an illustration

of the series, the remarkable properties of this composition and its interesting behavior under heat-treatment.

Maximum hardness and tensile strength in this alloy are developed by drawing, or heating, at 1075° to 1100° F. and slowly cooling. The alloys are softened by quenching in oil or water from 1500° F.

In the soft or quenched condition its tensile strength and hardness are about the same as those of hot-rolled Monel Metal itself, but when hardened its properties are comparable to those of a heat-treated alloy

TABLE 9.—*Comparison of Properties of Monel Metal with Those of Heat-treated Steel*

Metal	Proportional Limit, Lb. per Sq. In.	Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent	Reduction of Area, Per Cent	Brinell Hardness, 3000 Kg.
Nickel-chromium steel (S.A.E. No. 3330) oil-quenched from 1450° F. and drawn at 875° F.....		150,000	180,000	16	58	350
Aluminum-Monel Metal						
Full hard.....	100,000	120,000	160,000	20	30	330
Medium hard.....	80,000	100,000	140,000	30	40	275
Soft.....	25,000	35,000	90,000	50	65	140
Hot-rolled Monel Metal.....	30,000	45,000	90,000	40	65	150

steel, as shown by the figures in Table 9. The modulus of elasticity values are: tension, 26,000,000; torsion, 9,500,000.

These alloys can be hot-rolled or cold-rolled and hot-forged between 2100° F. and 1700° F.; they can be machined by the methods recommended for Monel Metal when their hardness is not greater than 300 Brinell.

The mechanism of the hardening by heat-treatment is not yet entirely clear, but undoubtedly is related to phase transformations occurring between 1100° and 1500° F. involving probably the precipitation in very finely dispersed form of a compound, or compounds, of aluminum, copper and nickel—possibly the solid solution  $\text{NiAl-Cu}_2\text{Al}$  described by Austin and Murphy<sup>6</sup>.

#### ACKNOWLEDGMENTS

The authors desire to acknowledge gratefully the sympathetic cooperation of Dr. J. F. Thompson, Mr. A. J. Wadhams and Mr. A. S. Shoffstall of The International Nickel Company, Inc., who have been instrumental in promoting investigation and development of these interesting alloys.

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## DISCUSSION

(Wheeler P. Davey presiding)

T. S. FULLER, \* Schenectady, N. Y. (written discussion).—This paper is sure to be of very great interest to those in search of alloys having valuable and unusual properties. The writer knows of no other series that possesses the combination of physical, chemical and magnetic properties shown by the alloys described. A nonmagnetic metal, having a high resistance to corrosion and showing tensile strengths up to and including 160,000 lb. per sq. in., and yield strengths up to 120,000 lb. per sq. in. with reasonable ductility, is sure to find wide and important uses in the arts.

It was the writer's privilege some years ago to study certain phases of this same alloy series. The results of his work in general were in agreement with those of Merica and Mudge. In the matter of the importance of the carbon content of the alloys, however, the writer was forced to conclusions quite different from those of the present authors. Merica and Mudge have stated that the carbon content is not essential. The writer prepared four alloys made to contain iron, 2.5 per cent; manganese, 1.5 per cent and aluminum, 2.5 per cent, the balance being nickel and copper in the ratio of 2:1. The carbon content of the four alloys was purposely varied and determined, and found to range from 0.16 to 0.26 per cent. The physical properties corresponding to the four different carbon contents after heating 6 hr. at 600° C. are shown in Table 10. Not only the results of these four heats containing 2.5 per cent

TABLE 10.—*Physical Properties of Four Aluminum-copper-nickel Alloys*

C	Ultimate Strength, Lb. per Sq. In.	Elastic Limit, Lb. per Sq. In.	Reduction of Area, Per Cent
0.16	95,000	54,000	65
0.21	144,000	103,000	51
0.23	145,000	101,000	51
0.26	136,000	92,000	

aluminum, but also the evidence furnished by many of the 75 alloys studied in this investigation, convinced the writer that where an aluminum content of 2.5 per cent is concerned the carbon content is of paramount importance.

The aluminum contents of the alloys reported by Mudge and Merica are somewhat higher, and it may be that with these alloys the role of carbon becomes less important.

\* Research Laboratory, General Electric Co.

TABLE 11.—Heat-treatment and Properties of Aluminum-Monel as Tested at Watertown Arsenal

Specimen No.	Diameter, In.	Heat-treatment		Hardness			Proportional Limit, 1000 Lb. per Sq. In.	Yield Strength, 1000 Lb. per Sq. In.		Elongation, Per Cent	Red. of Area, Per Cent	Notch Tensile Charpy, Ft.-lb.	Diameter Tensile Test Specimen, In./
				Brinell		Rockwell C							
		Deg. C.	Hr.	3000 Kg.	50 Per Cent R.	150 Kg.		Set 0.2 Per Cent	Set 0.5 Per Cent				
1	1½	Hard*			311		164		141	17	30	32	0.252 L and 0.125 T
2	2	Hard*		302	286	29	161		139	13	19	53.3	0.125 T
3	2	Soft*		166	167	11	151.6		106.0	21.4	37.6	44.1	0.357 T
3-1 <sup>a</sup>		598	3	269	269	25	93.8			47.5	66.7	81.1	0.125 T
3-2		598	2.5	302	302	30	98.4		46.1	48	52	56.4	0.357 T
3-3		598	5.5	311	305	29							0.125 T
4-1	1½	Soft*			187		101.0		68	32.0	66.6		0.252 T
4-2		593	7	299	299	29 ± 3	151.0		116	25.0	47.0		0.357 T
4-3		593	7	280	280	24.5	142.5		102.0	28.6	47.0		0.357 T
4-4		593	7	302	302	30.5	149.5		99.5	25.7	54.4		0.357 T
4-5		593	7	305	305	27.5	150.5		113.5	25.0	49.0		0.357 T
5-1	3½	Soft*			149	7	99.0		113.5	51	57		0.357 T
5-1-1 <sup>a</sup>		598	5.5	340*	340*	36.5	108.0		44.5	17.9	26.0		0.252 T
5-1-1 <sup>a</sup>		598	5.5	299	299	28.5	147.0		106.6	21.4	29.4		0.357 T
5-1-2 <sup>a</sup>		598	2										0.357 T
5-1-2 <sup>a</sup>		598	5.5										0.357 T
5-1-2 <sup>a</sup>		642	2	317		30.0	157.0		116.0	21.1	28.4		0.357 T
2	True breaking stress, 217,000 lb. per sq. in.; elongation, 0.30 in. in 1.4 in.												
3	True breaking stress, 202,000 lb. per sq. in.; elongation, 0.66 in. in 1.4 in.												

<sup>a</sup> Electric furnace.<sup>b</sup> Oil furnace.<sup>c</sup> Commercial treatment.<sup>d</sup> A = air, F = furnace.<sup>e</sup> Machine with great difficulty.

/ T = transverse, L = longitudinal.

P. R. KOSTING, \* Watertown, Mass. (written discussion).—Watertown Arsenal is always interested in engineering materials with corrosion-resisting properties. It therefore investigated the properties of Aluminum-Monel. The results obtained are given in Table 11.

An observation that still interests the Arsenal is that when corroded in dilute sulfuric acid the hard specimen No. 1, which was drilled with extreme difficulty with a plain carbon drill, rapidly increased in corrosion rate. If the corrosion rate of Monel Metal is taken as 100, the corrosion rate of Aluminum-Monel No. 1 increased from 120 for the first period to 665 for the third period. Cracks opened up around the drill hole.

W. A. MUDGE (written discussion).—With respect to the values cited by Dr. Fuller, the suggestion is advanced that a variation in finishing temperature on forging may be more responsible for his results than the percentage of carbon. It would be of further interest to know whether all of Dr. Fuller's alloys were softened previous to hardening, so as to remove all effects of forging. The authors have found that alloys with as little as 2.5 per cent of aluminum give little hardening, regardless of carbon content, if they are softened by quenching from 1450° to 1500° F. before the hardening treatment at 1100° F.

Dr. Kosting's mechanical values, some of which were obtained jointly with one of us, are a valuable addition to the paper. We believe that the corrosion rate of his sample No. 1, which was drilled in the hard (heat-treated) condition, was aggravated by the strains set up during the drilling operation, and that this apparent defect could be removed by a strain-relief treatment at 575° F.

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\* Chemical Engineer, Watertown Arsenal.

## Physical and Casting Properties of the Nickel Silvers

By T. E. KIHLEGREN,\* N. B. PILLING† AND E. M. WISE,‡ MEMBERS A.I.M.E.

(New York Meeting, February, 1935)

SYSTEMATIC data are presented on the relation of composition of nickel silvers to color, tarnish resistance, hardness and liquidus temperatures, for alloys containing up to 30 per cent nickel and 50 per cent zinc, further modified at certain nickel and zinc contents by 0 to 8 per cent of tin and 0 to 10 per cent of lead. Attention has also been directed, using a still more limited range of alloys, toward a study of tensile properties and such casting properties and characteristics as fluidity, shrinkage and pressure tightness. In some of these, rather broad ranges of composition are dealt with; in others, it has been expedient to focus attention on the Federal Specification 20 per cent nickel silver casting alloy, WWP-541.

### INTRODUCTION

The demand for an alloy essentially white in color, which could be cast and worked by simple methods and which possessed strength and corrosion-resisting properties superior to the usual brasses, led to the discovery and early use of cupronickel alloys containing zinc, and sometimes tin, lead and other metals. This type of alloy was generally known as German silver until the war, when the term "Nickel Silver" became generally accepted. The element principally responsible for the white color of the alloy and for its strength and corrosion resistance is nickel, which may constitute from 8 to 30 per cent of the alloy. The functions of the other elements will be described later. The manifold uses of nickel silver are largely due to its color, corrosion resistance, ease of casting, fabrication, joining and rather moderate cost. In many instances the alloy is finished by grinding and polishing while in others it may be finished with a silver or nickel plus chromium plate. Electroplates applied to a nickel silver base behave more satisfactorily than those applied to the softer and less resistant alloys, and owing to the white color of the underlying metal the article will retain a pleasing appearance despite local failures of the plating.

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\* Metallurgist, Research Laboratory, The International Nickel Co., Bayonne, N. J.

† Manager, Research Laboratory, The International Nickel Co.

‡ Assistant Manager, Research Laboratory, The International Nickel Co.



Recently new interest has been shown in the architectural applications of nickel silver, because of the ranges of color that can be secured and its availability in extruded, rolled, drawn and cast sections, and particularly because of its availability in tubular form. These factors have made it preeminent for plumbing fixtures of the highest grade, for a variety of marine fittings and for certain types of food-processing equipment, while the resistance to impingement attack of the alloys of higher nickel and

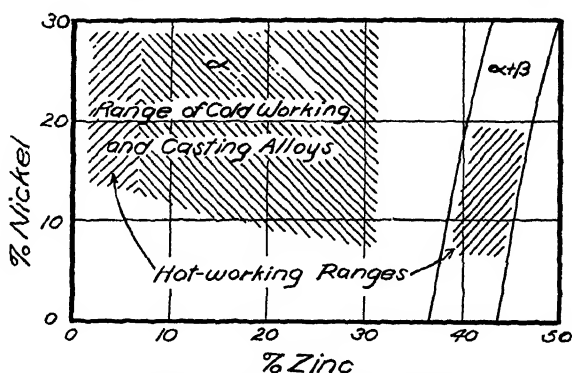


FIG. 1—COMPOSITION RANGES OF NICKEL SILVERS.

low zinc content has led to their use for resisting the attack of the cooling waters employed in steam condensers.

At the outset, it may be well to consider the three fundamentally different types of nickel silver alloys that are employed commercially and which may be utilized as components of a finished assembly involving cast elements. Each of these groups may be further subdivided according to its nickel content and resulting color, a subject that will be discussed later.

The basis of the subdivision is the method of forming to which the alloy is most amenable: (1) cold working, (2) hot working and (3) casting.

*Cold-working Alloys* may contain from 5 to 30 per cent of zinc and, where machinability is required, from 1 to about 3 per cent of lead. The nickel content will range from about 10 to 30 per cent, depending upon the color, strength and tarnish resistance required. The structure of this type of alloy is a simple alpha solid solution similar to that of copper or alpha brass, but the strength is considerably higher than that of a simple alpha brass of similar zinc content.

*Hot-working or Extruding Alloys* may contain from 38 to 45 per cent of zinc and from 8 to 18 per cent of nickel. These alloys contain varying amounts of alpha and beta, depending upon the composition and heat treatment. In addition, certain of the cold-working alloys containing less than 10 per cent of zinc and sometimes a small amount of manganese can be worked hot as well as cold.

*Casting Alloys* may contain from 12 to about 30 per cent of nickel, usually from 5 to 15 per cent of zinc, from 2 to 10 per cent of lead and up to about 6 per cent of tin. Zinc lowers the melting point and probably also tends to minimize porosity due to gas evolution. Lead aids in producing hydraulic tightness and tin substantially hardens and strengthens the alloy; both lower the melting point and promote fluidity.

The fields of hot-working, cold-working and casting alloys are broadly outlined in Fig. 1.

The following important characteristics of the nickel silver alloys are considered in detail:

1. Color and color matches between cast and wrought alloys.
2. Tarnish resistance.
3. Hardness.
4. Liquidus temperatures.
5. Fluidity.
6. Shrinkage: freezing, solid, patternmaker's allowance.
7. Effect of variations in deoxidation procedure on soundness of cast nickel silver.
8. Tensile properties of Federal Specification and related 20 per cent nickel silver alloys.

### COLOR

The importance of color as an architectural adjunct can hardly be overestimated. Not only is color harmony frequently desired in composite metal structures, but at times subdued color contrasts are demanded, results which can be secured easily in nickel silver alloys of appropriate composition. It has been thought desirable to develop the relations between color and composition of an extensive series of copper-nickel-zinc alloys, in which the nickel content ranged from 15 to 25 per cent and zinc from 0 to 50 per cent. For certain chosen zinc levels the effect of up to 8 per cent of tin and 10 per cent of lead on color has also been studied.

In determining the relation between composition and color in these alloys it was found that photometric methods were not very useful, partly because the color tints are delicate and particularly because of the difficulty in visualizing the data so obtained. The results of careful visual observations are thought to be more useful, and such results, presented in diagrammatic and descriptive form, have been utilized herein. It is believed that this treatment will give sufficient information so that an intelligent selection of alloys can be made that will insure a pleasing harmony of color between the components of composite metal structures involving extruded, wrought and cast elements.

Briefly, it may be stated that nickel is the most important element in developing whiteness. Zinc in the presence of sufficient nickel also exerts

a definite though less vigorous decolorizing influence. Tin and lead in the amounts in which they are usually present in nickel silver exert a rather secondary effect.

The influence of the various components of nickel silver on color has been followed in some detail by examining clean chip samples in diffused daylight. Since the nickel silvers are essentially copper-nickel-zinc alloys, the colors of which are only mildly modified by the tin and/or lead which may be added to gain some advantage in casting or processing facility, the relation between color and composition of the ternary alloys is of fundamental importance.

*Colors of Copper-nickel-zinc Alloys.*—This relationship between composition and color is schematically depicted in Fig. 2. It should be realized, of course, that there is no sharp transition from one field to the

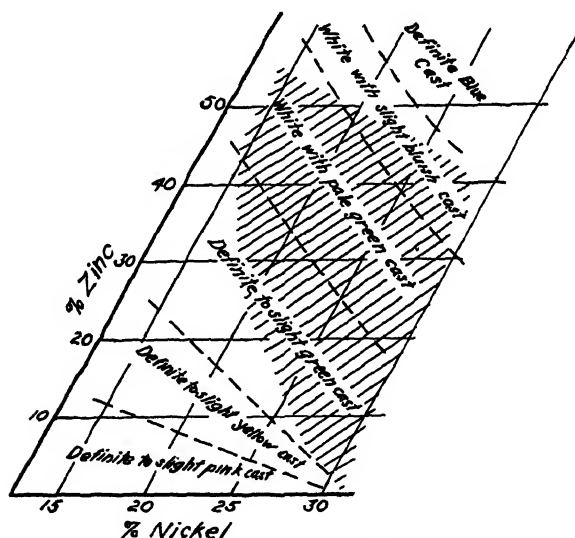


FIG. 2.—COLOR TRENDS OF SIMPLE COPPER-NICKEL-ZINC ALLOYS.  
Shaded area indicates sensibly "white" alloys.

next, the colors merging gradually. The shaded area indicates the region of approximately "white" alloys; at 15 per cent nickel, about 45 per cent of zinc is required to enter the region of "white" alloys, while at 20 per cent nickel, about 30 per cent zinc is required, and at 30 per cent nickel, only about 5 per cent zinc.

Except at extremely high zinc contents (40 to 50 per cent), at which definite blue casts are introduced at the higher nickel contents, the effect of nickel at a given zinc level is to decrease the intensity of the color tone; i.e., to make the alloy whiter. Particularly notable is the marked increase in whiteness when the nickel is increased from 15 to 20 per cent.

*Effect of Auxiliary Elements on Color of Nickel Silver.*—Generally it may be stated that tin, in amounts that would seem permissible from considerations of machinability, castability, hardness, etc., may be considered to play a rather secondary part in color changes of the nickel silvers. The addition of tin up to 4 per cent tends to mask the pink east of the cupronickels, and a further slight decolorizing effect is noticed with 8 per cent of tin. In the presence of 15 per cent of zinc, tin accentuates

TABLE 1.—Federal Specification WWP-541

	Desired Per Cent	Maximum Per Cent	Minimum Per Cent
Nickel.....	20		19
Copper.....	65		62
Zinc.....	6	10	
Tin.....	4		2½
Lead.....	5	6	
Manganese.....		1	
Iron and other impurities.....		1	

the yellow-green or green tints, but the effect is rather small, while with 30 per cent of zinc, tin exerts a very mild effect on color.

Lead has slight effect on color, as might be expected from its insolubility in the copper-nickel-zinc matrix at room temperature.

*Color Matches with a Commercial Wrought 20 Per Cent Ni, 5 Per Cent Zn Alloy.*—In view of the wide use of wrought 20 per cent nickel silver (Ambrac) pipe in conjunction with cast elements of the "Federal Specification" type of 20 per cent nickel silver in plumbing fixtures, a somewhat detailed study was made to develop the relation between the dominant color-controlling elements, nickel and zinc, to obtain casting alloys matching this material. Specification limits of the Federal Specification alloy are given in Table 1.

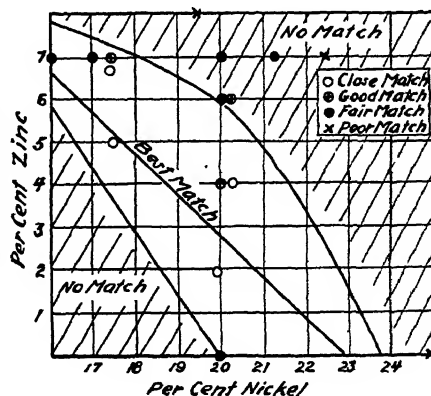


FIG. 3.—COMPOSITION LIMITS OF CASTING ALLOYS TO MATCH 20 PER CENT NICKEL SILVER PIPE. ALLOYS CONTAIN 2 PER CENT SN, 4 PER CENT PB.

In developing the color matches for the wrought 20 per cent nickel silver, casting alloys containing varying amounts of nickel and zinc with 2 per cent of tin and 4 per cent of lead were used. However, small variations in tin and lead will not markedly alter the color relations between nickel and zinc, which are shown in



GRAY

50Ni									
	18-8			60Ni	Monel				
25Ni 30Zn 8Sn						80Ni- 20Cu			
35Ni 5Zn	40Ni	45Ni							
		Inconel				Ever- brite			
25Ni 15Zn 10Pb	35Ni 30g Ambrac			90Ni					
25Ni 15Zn 5Pb		30Ni		25Ni	25Ni 5Pb				
25Ni 15Zn	Nickel								
20Ni 20Ni 15Zn 15Zn 4Sn 4Sn 5Pb 5Pb	225 Ni 10Zn	25Ni Ni 10Zn	225 Ni 8Zn 25Sn 4Pb	185 Ni 8Zn 25Sn 4Pb	20Ni 105 7Zn Ni 7Zn 0.2Zn 25Sn 5Zn 4Pb	20Ni 20Ni 6Zn 4Zn 25Sn 25Sn 4Pb 4Pb			
	20Ni 15Zn 5Pb	185 Ni kel Sil- ver	20Ni 15Zn		175 Ni 7Zn 10Zn 25Sn 25Sn 4Pb	185 Ni 7Zn 22Sn 25Sn 4Pb	175 Ni 0.2Zn 25Sn 4Pb	20Ni 20Ni 0Zn 4Sn	
					175 Ni 7Zn 25Sn 4Pb	185 Ni 7Zn 25Sn 4Pb	175 Ni 7Zn	20Ni	185 Ni
15Ni 15Zn 8Sn		15Ni 15Zn 2Sn	15Ni 15Ni 15Zn 15Zn 5Pb 5Pb		15Ni 10Zn			15Ni 5Zn	15Ni 15Ni 5Pb 5Pb

Whitest  
Alloys

PINK

FIG. 4.—(CONTINUED).

Fig. 3. The colors in this case were those observed in freshly polished blocks, not chip samples. The best matches are to be had in alloys containing 16 to 23 per cent of nickel and in which the sum of the nickel and zinc is constant at about 23 per cent, with 2 per cent tin and 4 per cent lead. The areas of tolerable match broaden out when nickel lies between 18 and 22 per cent; if this is disregarded, the zinc content in alloys containing 16 to 22 per cent of nickel, 2 per cent tin and 4 per cent lead, which, freshly polished, will give an acceptable color match with 20 per cent nickel 5 per cent zinc pipe, may be defined by the relation:

$$\text{Per cent Zn} + \text{per cent Ni} = 22 \text{ to } 24$$

*Matching Commercial and Experimental Alloys.*—A matching chart was obtained by grouping a large number of buffed blocks of experimental nickel silvers of widely varying compositions and of commercial alloys. The results are presented in Fig. 4. This permits not only an estimate of the general relations between color and composition, but may be used to choose casting alloys which when freshly polished will yield a good match to various commercial wrought alloys, in conjunction with which they may be used.

The polished blocks were viewed in diffused northern daylight and arranged according to their color. It was found that a satisfactory grouping could be made in a rectangular domain, the lower right corner of which contained alloys with pink tints; the lower left yellow; the upper left blue; the upper right gray, the "white" region being near the center of the plot. With this arrangement, deepness of tint is suggested by distance from the "white" center, and color by direction. For example, a distinctly green alloy, if such should exist, would lie on the border of the plot between the yellow and blue corners.

In arranging the samples, an effort was made to separate them by distances proportional to their differences in color, or at least by the "grating tendencies" of such color differences upon the sensibilities of the observer. In the figure, alloys in the same space constitute close or exact matches and those in adjacent squares match well. Alloys located on a diagonal match less closely than those equally removed in a horizontal or vertical direction. In general, clean polished alloys two squares apart vertically or horizontally or one square apart diagonally can be used in juxtaposition satisfactorily. This color grouping was arrived at by observation in a room illuminated by daylight. Under less critical conditions of illumination and under artificial light the tolerance of match will be considerably greater.

Colors are largely relative and an alloy that appears white when alone may appear to possess a distinct color cast when placed close to another apparently white alloy. Therefore the precise location of the region of "whitest" alloys is rather difficult. The square marked in the center of

Fig. 4 indicates this zone, based on the weighted average of reactions of a number of observers.

Where tarnishing occurs, some divergence in color may develop in alloys initially similar in color, particularly when the nickel content of the two alloys differs considerably. This will be dealt with below.

#### EFFECT OF COMPOSITION ON TARNISH RESISTANCE

The resistance of nickel silver alloys to tarnishing is of some importance in spite of the fact that periodic cleaning will be required in any case to

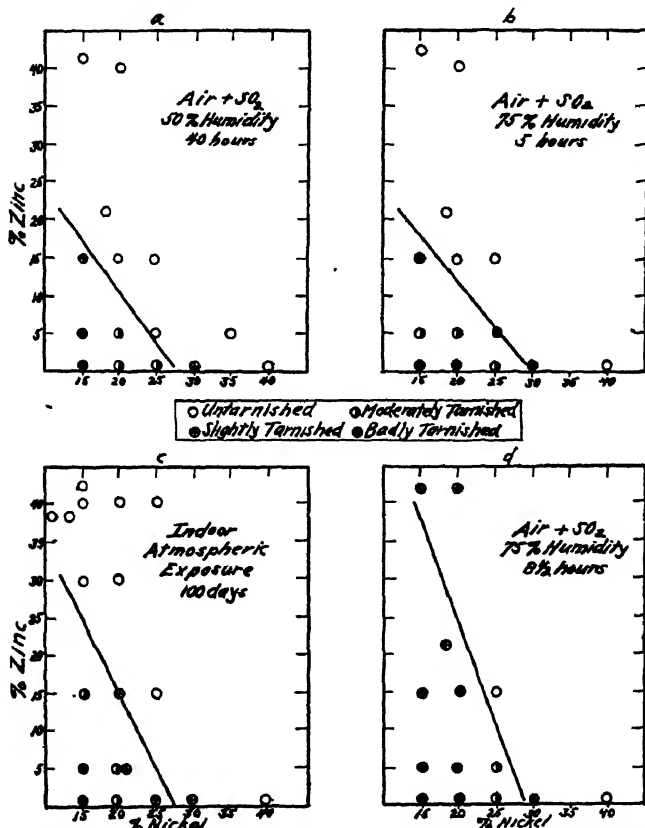


FIG. 5.—ACCELERATED AND INDOOR ATMOSPHERIC TARNISH TESTS ON COPPER-NICKEL-ZINC ALLOYS.

remove dirt and other accretions, and it is particularly important that the component parts of a structure retain sensible color harmony even if some tarnishing occurs. For this reason studies were made of the tarnish behavior of a wide variety of alloys polished and allowed to remain exposed indoors to the atmosphere of the laboratory for over three months. Photometric measurements were made from time to time to follow the change in reflectivity. These are not presented here, but a



brief summary of the results of visual examination of the simple copper-nickel-zinc alloys is given in Fig. 5c. It is evident that while nickel is the dominant element in conferring tarnish resistance, zinc offers some aid, although the amounts required for effective results with nickel below 20 to 25 per cent restrict its use for many casting purposes. The high-zinc alloys, however, are appropriate for extrusion and forging purposes.

Accelerated tarnish tests are always desired, but the results of certain test procedures are difficult to interpret. These difficulties are believed to be least when air containing  $\text{SO}_2$  is employed and where the humidity is controlled; therefore tests were conducted with these reagents on specimens surfaced by fine grinding on fresh carborundum paper. The samples were placed in a chamber through which was passed a stream of

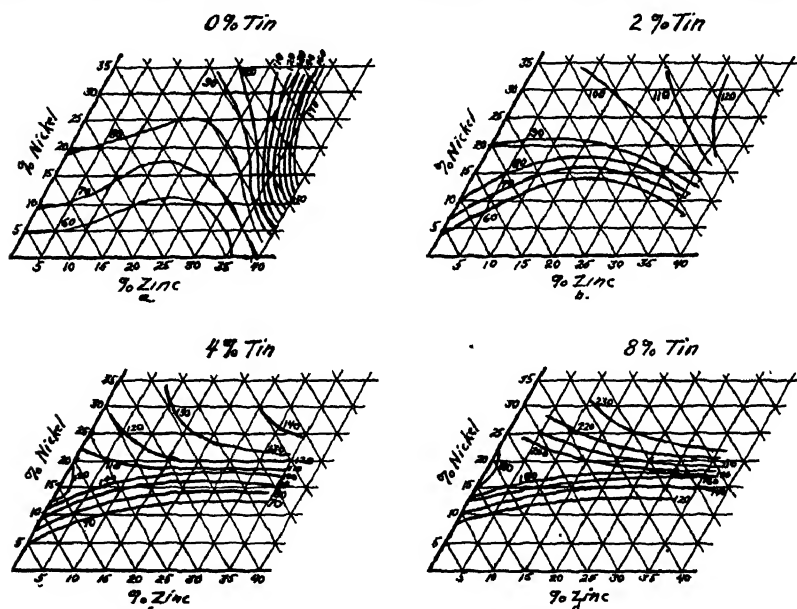


FIG. 6.—BRINELL HARDNESS OF SAND-CAST TIN-CONTENT NICKEL SILVERS.

air that had been bubbled through a saturated aqueous solution of sodium bisulfite and then through bottles containing solutions of sulfuric acid of concentrations appropriate to maintain a relative humidity of 50 or 75 per cent, as desired. The test was conducted at room temperature. The samples in the first experiment were examined after 40-hr. exposure at 50 per cent relative humidity, with the results indicated in Fig. 5a. The general relation between composition and tarnishing is somewhat similar to the long-time laboratory atmosphere exposure. Raising the humidity to 75 per cent increased the rate of attack about eightfold on the low-zinc and low-nickel alloys, so that the results of a 5-hr. exposure shown in Fig. 5b are similar to those of the preceding test. Increasing

the exposure to  $8\frac{1}{2}$  hr. at 75 per cent relative humidity resulted as shown in Fig. 5d, which indicates that the contribution of zinc to tarnish resistance is least with this more drastic test.

The behavior of the more complex alloys was also considered but will not be discussed in detail at this time. It may be noted, however, that the first small addition of tin offered some improvement in vulnerable alloys and that the effect of lead was rather slight. It is believed that this brief outline of the behavior of the nickel silvers will afford some guidance in the choice of alloys for appearance uses.

### HARDNESS OF CAST NICKEL SILVER ALLOYS

The hardness of an alloy frequently is important in the ultimate application of the material and in connection with machining and polishing

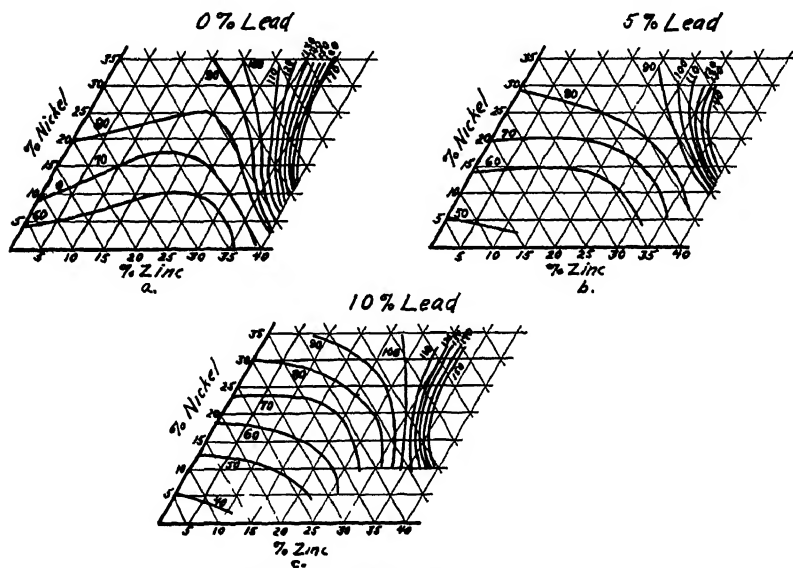


FIG. 7.—BRINELL HARDNESS OF SAND-CAST LEAD-CONTENT NICKEL SILVERS.

operations. A survey was therefore made of the influence of composition upon this property, as exhibited by well fed, dry sand-cast blocks ( $5\frac{1}{2}$  in. wide, 4 in. high and 1 in. thick), of a wide variety of possible casting alloys. The Brinell hardness of the block was obtained using a 1000-kg. load on a milled surface  $\frac{3}{4}$  in. from the bottom. The alloys were all melted in an Ajax furnace and were deoxidized with 0.05 per cent magnesium and 0.075 per cent phosphorus. The compositions noted are all based upon the weight of the components as charged. The results obtained for the simple copper-nickel-zinc alloys are shown in Fig. 6.

The hardness rises rather steadily with the nickel content from about 48 for copper to about 86 for the 30 per cent cupronickel and increased amounts of zinc up to about 20 to 25 per cent produce a slight softening;

this effect is somewhat anomalous and the reason for it is not entirely clear. A further increase in zinc generally results in an increase in hardness, rather slow at first and then much more rapidly as the beta field is entered.

*Effect of Tin.*—The effect of tin at levels of 2, 4 and 8 per cent upon the hardness of copper-nickel-zinc alloys is set forth in *b*, *c* and *d* of Fig. 6. In the presence of 2 per cent of tin, the relation between hardness and zinc and nickel content is similar to that of the tin-free alloy up to about 25 per cent zinc, except that the alloys containing in the neighbor-

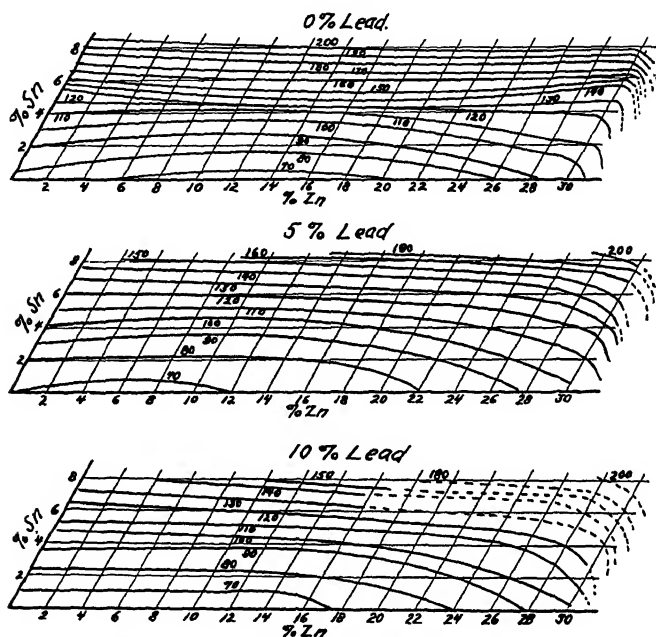


FIG. 8.—BRINELL HARDNESS OF SAND-CAST 20 PER CENT NICKEL SILVER CONTAINING TIN AND LEAD.

hood of 20 per cent nickel are from 10 to 15 points harder than in the 0 tin alloys. In the alloys containing 4 and 8 per cent of tin, a further increase in hardness occurs, and the effect on the hardness of increasing the percentage of nickel is more marked than in the previously considered alloys, and this effect is far more important than that due to considerable changes in zinc content.

*Effect of Lead.*—The effect of lead at levels of 0, 5 and 10 per cent upon the hardness of nickel silver castings is shown in Fig. 7. The general effect of increasing lead is to increase the hardening effects of zinc, owing in part to the fact that the actual copper content of the alloy is reduced by substitution of lead for copper, which results in the production of a harder matrix. The lead, dispersed throughout the solid alloy,

tends to soften the alloy, but this effect is partly counterbalanced by the action noted above.

*Cast 20 Per Cent Nickel Silver Alloys Containing Both Lead and Tin.*—The influence of variations in tin and zinc content upon the hardness of alloys containing 0, 5 and 10 per cent of lead with nickel constant at 20 per cent is shown in Fig. 8. As will be noted, the influence of zinc upon the hardness is slight up to a level depending largely on the lead content, and is mild at all times. In contrast to zinc, tin exerts a pronounced hardening effect, the hardening being most vigorous in the free

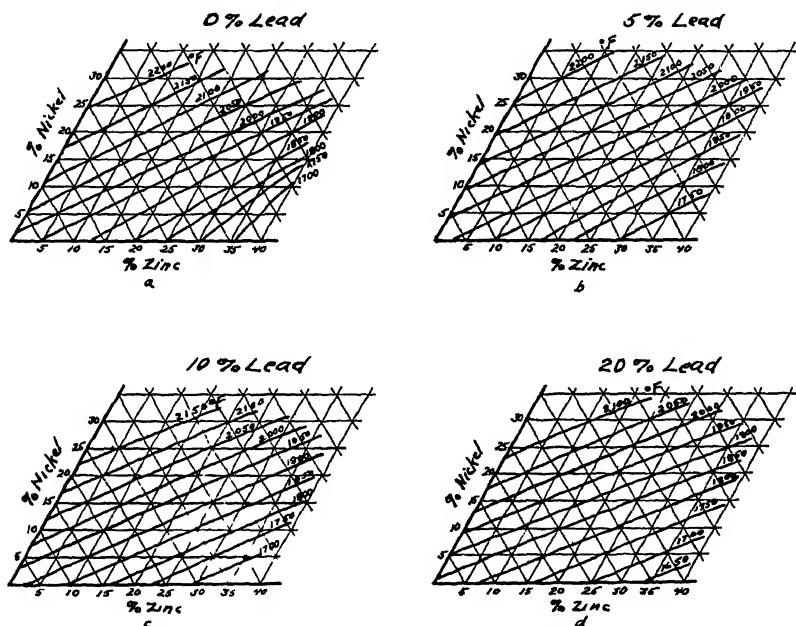


FIG. 9.—MELTING POINTS OF LEAD-CONTENT NICKEL SILVERS, DEGREES FAHRENHEIT. *a* relates to simple nickel silver alloys (Ni, Cu, Zn only); *b*, *c*, *d* relate to alloys containing 5, 10 and 20 per cent lead with nickel and zinc varied.

lead alloys. The hardening effect of tin is somewhat reduced in the presence of lead, partly due to the softening effect of the dispersed lead particles and perhaps partly to a decrease in the spontaneous age-hardening effects that occur during the cooling of the casting.

In view of the fact that fixed amounts of lead and zinc frequently are desired in casting mixtures, these graphs should be useful in providing a ready estimation of the amount of tin required to meet a particular hardness in a 20 per cent nickel alloy in a section of the dimensions considered.

#### LIQUIDUS TEMPERATURES

The lowest temperature at which the alloy is completely molten (the liquidus) was determined for a wide range of compositions by melting the

alloy and obtaining cooling curves with an immersed sheathed platinum-rhodium platinum thermocouple. The results are shown in Figs. 9 and 10. A similar method of plotting was employed for the alloys containing 0, 2, 4 and 8 per cent of tin shown in Fig. 10.

Where both lead and tin are present, together with nickel, copper and zinc, an adequate estimate of the liquidus can be arrived at by assuming that the lowering of the melting point is roughly additive. Obviously, pouring temperatures considerably higher than the liquidus temperature

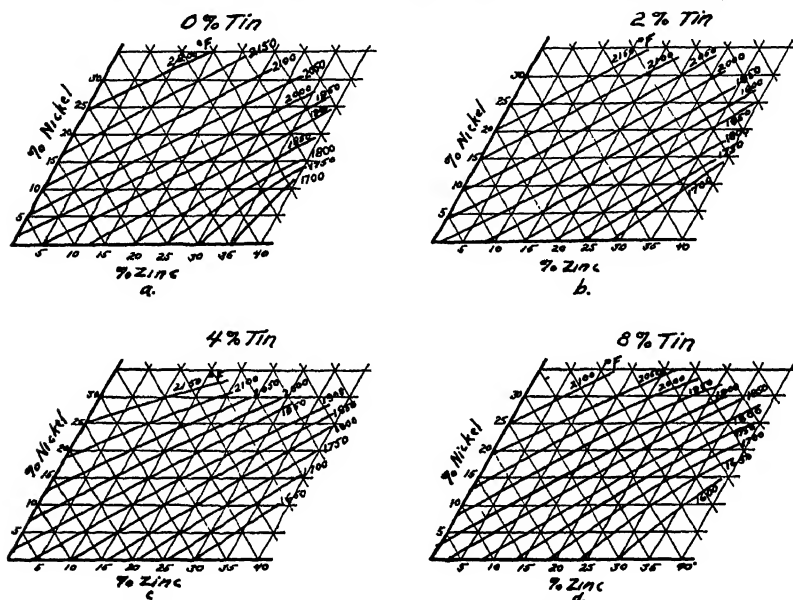


FIG. 10.—MELTING POINTS OF TIN-CONTENT NICKEL SILVERS, DEGREES FAHRENHEIT.

are required in practice, the amount of superheat depending upon the type of casting being run. It is believed that a knowledge of the true melting point, particularly of its variation with composition, will be useful when changing alloy composition and in meeting particular requirements as to melting point, such as an estimate of the amount of lead, tin and zinc that should be added to maintain a constant melting point with an increase in nickel content.

#### FLUIDITY OF NICKEL SILVER ALLOYS

The fluidity of a considerable range of nickel silver alloys was determined by measuring the length of spiral that could be cast at known temperatures in green sand. The design of the fluidity test casting is shown in Fig. 11. This is a modification of the pattern described by Pilling and Kihlgren<sup>1</sup>, the principal change being the addition of a sump

<sup>1</sup> N. B. Pilling and T. E. Kihlgren: Casting Properties of Nickel Bronze. *Trans. Amer. Foundrymen's Assn.* (1932).

at the bottom of the pouring basin to minimize velocity-head effects. The gate is located about 1 in. up from the bottom of the pouring basin, arranged to prevent any wash of metal into the gate and spiral prior to the advent of the main stream. The revised pattern constitutes an improvement over the previous design and has been found useful in developing

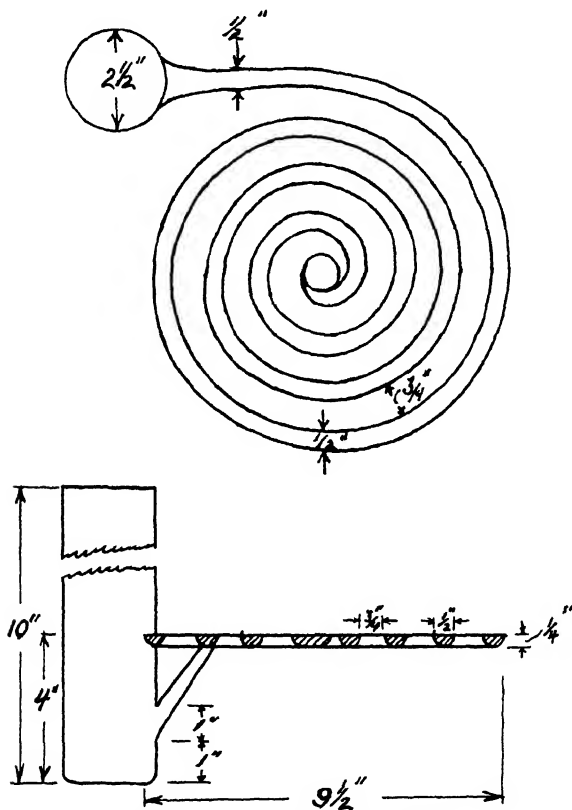


FIG. 11.—FLUIDITY TEST CASTING.

fluidity data for the nickel silvers. The general method of procedure of test was described in the paper cited. The melts weighed about 150 lb. each and were made under a charcoal cover in a clay-graphite crucible. The melts were made in an oil-fired crucible pit furnace and were deoxidized with 0.05 per cent phosphorus 0.05 per cent magnesium.

The temperature of the melt was determined by an immersed bare chromel-alumel thermocouple. The observed pouring temperatures were based on the millivolt-temperature calibration supplied by the manufacturer, and represent the temperature of the surface of the melt. Comparisons were made over a range of several hundred degrees Fahrenheit between the temperatures in the center of the melt as determined by a sheathed platinum-rhodium platinum thermocouple and

that indicated by a bare couple, which indicated that the latter was approximately 75° below the former. A correction of this amount has been made on the graphs, so that the temperatures indicated thereon are approximately the actual temperatures of the melt. This difference

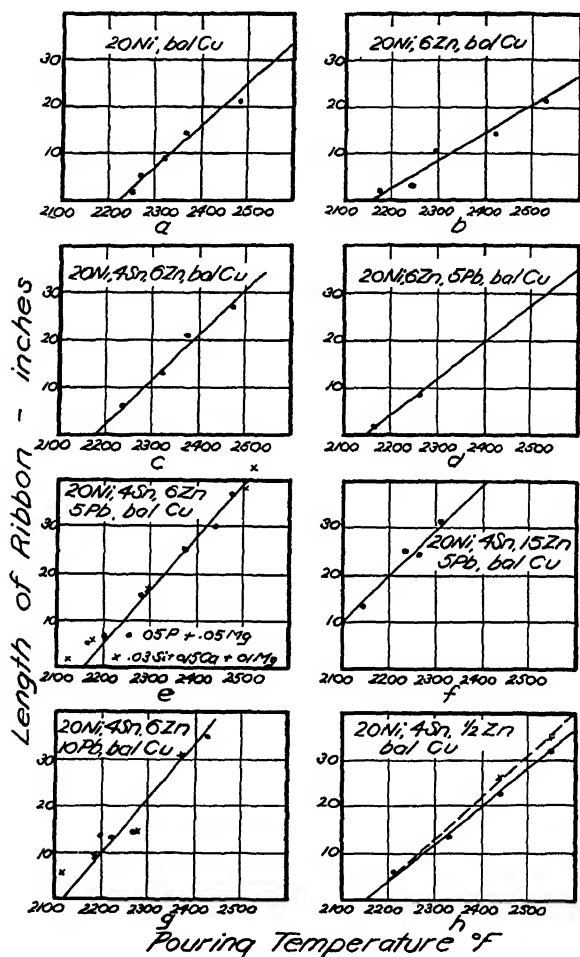


FIG. 12.—FLUIDITY OF NICKEL SILVER CASTING ALLOYS.

between the observed temperatures using bare chromel-alumel immersion thermocouples and the actual pot temperatures should be borne in mind in using this method to obtain pouring temperatures. It may be noted in passing that some bare immersion couples commercially available appear to embody a correction of about the amount found necessary.

The 20 per cent nickel alloy was employed because this amount of nickel is required for a number of reasons, including color and tarnish resistance, and also because specifications frequently demand it.

In Fig. 12 the spiral length-temperature ( $T$ - $L$ ) curves are shown for the various mixtures. The  $T$ - $L$  curve for the 20 per cent cupronickel is shown in Fig. 12a and the effect of separate and joint additions of tin, zinc and lead in amounts of 4, 6 and 5 per cent respectively in 12b, c, d, e and h. These amounts were used because of their occurrence in the Federal Specification type of 20 per cent nickel-silver casting alloy. In g the fluidity curve for a modification of the above alloy containing 10 per cent of lead is shown. This alloy was included because it is less sensitive to inadequate gating than the similar alloy with 5 per cent of lead. Fig. 12f shows the  $T$ - $L$  relationship obtained for a 15 per cent zinc nickel silver containing 4 per cent tin and 5 per cent lead.

In all cases a straight line has been drawn through the points and has been extended until it cuts the temperature axis at a point considered to represent zero fluidity. The temperature corresponding to this intersection will be termed "apparent zero fluidity." Actually the relation does appear to be substantially linear for the alloys considered, over most of the temperature range. There is some tendency for alloys containing tin plus lead to show some curvature at the lower temperatures, which

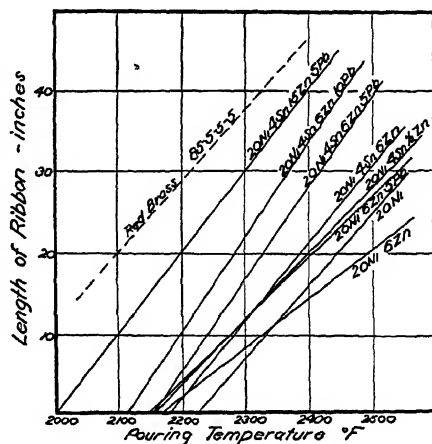


FIG. 13.—FLUIDITY OF NICKEL SILVER CASTING ALLOYS.

may indicate some feeding ability below the liquidus temperature. The  $T$ - $L$  relationship for the 20 Ni, 4 Sn, bal. Cu alloy is shown in curve h. The dotted curve is included because two of the spirals showed long tapering ends instead of the bluntly rounded ends obtained with the other alloys, although there was no indication that this was due to gas extrusion.

The  $T$ - $L$  curve for the alloy conforming to the desired composition for the Federal Specification alloy is shown in Fig. 12e. Two deoxidation treatments were used, involving the addition of 0.05 per cent Mg + 0.05 per cent P and 0.03 Si + 0.015 Ca + 0.01 Mg (added as a copper-base alloy) respectively. For these two treatments the  $T$ - $L$  relationships are apparently the same. The effects of other deoxidizers and different percentages of the additions mentioned has not been investigated.

To facilitate comparisons between the various alloys, the results have been assembled on a single plot in Fig. 13, which permits a ready comparison of fluidities of the several alloys at chosen temperatures or perhaps, more importantly, indicates directly the temperatures at which these alloys will possess the same fluidity. This should aid in estimating



changes of pouring temperature that may be required to compensate for the change in fluidity of a casting alloy resulting from a variation in lead, tin or zinc.

Owing to the varying melting points of the alloys, the "apparent zero fluidity" temperatures cover a considerable span. The results have been re-plotted with a common origin in Fig. 14, bringing out rather surprising differences in the behavior of the several alloys when cast at a constant superheat (above zero fluidity). This figure discloses that zinc reduces

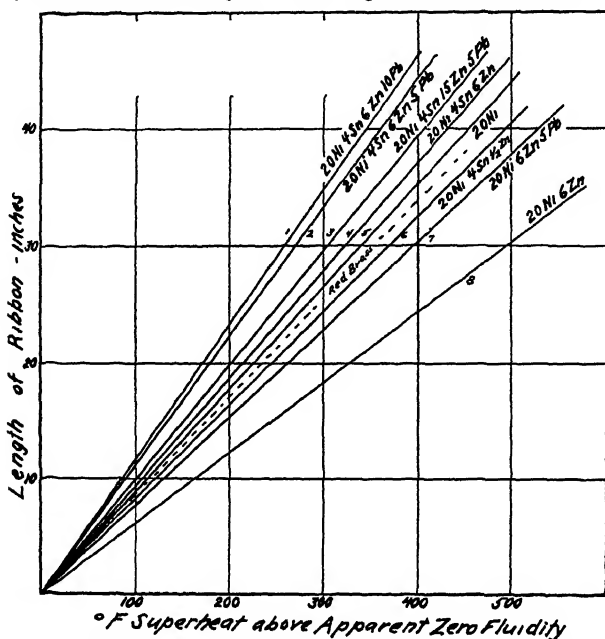


FIG. 14.—RELATIVE FLUIDITY OF NICKEL SILVER CASTING ALLOYS.

the temperature coefficient of fluidity, or more briefly the "fluidity coefficient," as indicated by comparison of the slope of curves 5 and 8. In the presence of 6 per cent of zinc, both tin and lead increase the fluidity coefficient and when present together in amounts of 4 and 5 per cent respectively exhibit a somewhat additive effect. Increasing the lead from 5 to 10 per cent with tin and zinc constant (curves 1 and 2) has little further effect, the slopes being nearly alike. Increasing the zinc from 6 to 15 per cent (curves 2 and 3) effects a moderate decrease in the fluidity coefficient. In the absence of zinc, tin apparently has no fluidizing effect on 20 per cent cupronickel; in the presence of considerable amounts of zinc its fluidizing effect is pronounced. The presence of zinc in appreciable amounts probably prevents the formation of tin oxides which may decrease the fluidity.

For comparison, the fluidity curves for red brass are shown on Figs. 13 and 14 by dotted lines. It may be compared with the 20 Ni, 4 Sn, 6 Zn,

5 Pb, bal. Cu alloy, from which it differs chiefly in nickel content. Apparently nickel exerts a fluidizing effect, which is masked by the increase in melting point accompanying the introduction of nickel into the alloy.

### SHRINKAGE

Each metal or alloy has certain inherent characteristics which cannot be altered without change of composition. The contraction in volume as a metal cools from a temperature above the liquidus to room temperature is one of these. The shrinkage may be roughly divided into three components: (1) the change in volume occurring in the liquid state, termed liquid shrinkage; (2) the contraction in volume during cooling from liquidus to solidus, called freezing (or solidification) shrinkage; and (3) that occurring in the solid state, known as solid shrinkage. The harmful effects of liquid shrinkage can be minimized by proper attention to feeding and to pouring temperatures. Solid shrinkage is satisfactorily compensated by using the proper patternmaker's allowance for shrinkage. The effects of freezing shrinkage, however, are not thus easily minimized. Obviously, it is impossible to feed metal throughout the casting after freezing is well under way, but considerable control can be exercised over the manner in which solidification shrinkage is distributed, if not its actual magnitude, as later will be demonstrated.

*Liquid Shrinkage of Nickel Silver.*—No data are at present available for this important factor. Practical experience indicates that gates and risers two to three times the weight of those employed for red brass are desirable. When such precautions are taken, the difficulties in production of sound castings are considerably lessened.

TABLE 2.—Freezing Shrinkage of Nickel Silver

Composition of Alloy, Per Cent					Total Volume Shrinkage, Per Cent	Linear Shrinkage, Per Cent	Freezing Shrinkage, Per Cent
Cu	Ni	Zn	Sn	Pb			
80	20				12.5	2.24	5.8
bal.	20		4		12.7	2.04	6.7
bal.	20	6	4		13.3	2.19	6.7
bal.	20			5	13.0	2.23	6.3
bal.	20	6	4	5	12.1	1.77	6.8
bal.	20	6	4	10	12.2	1.98	6.3
bal.	20	15			12.1	2.19	5.5
bal.	20	15	4	5	12.1	1.88	6.5
Red brass					10.8	1.44	6.5

*Freezing Shrinkage.*—Using the method described in a previous publication<sup>2</sup>, the freezing (or piping) shrinkage (which is the volume

<sup>2</sup> N. B. Pilling and T. E. Kihlogren: A Method for Study of Shrinkage and its Distribution in Castings. *Trans. Amer. Foundrymen's Assn.* (1932).

change occurring as metal cools from the liquidus to the solidus) was determined for several alloys (Table 2), all of which exhibit freezing shrinkages of the order of 6 to 7 per cent, though varying considerably in composition and in casting behavior.

In order to obtain some idea of the manner in which the shrinkage occurred, the castings were split axially. It is interesting to note the

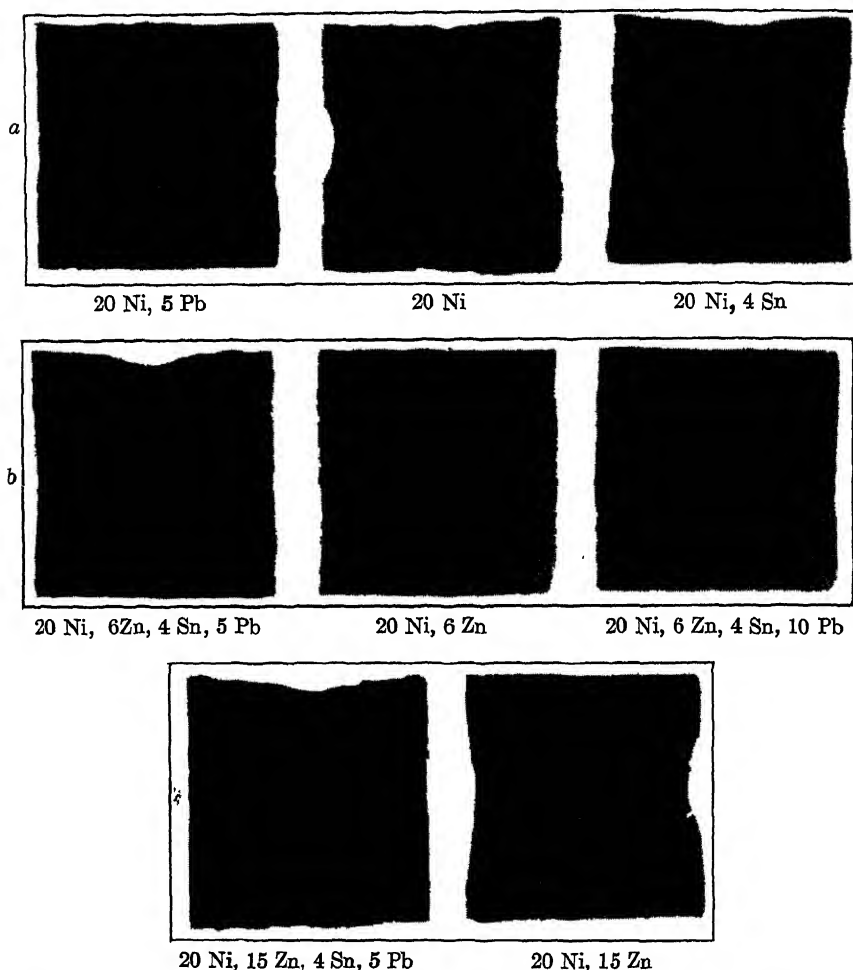


FIG. 15.—DISTRIBUTION OF SHRINKAGE PIPE IN UNFED CYLINDERS POURED AT FREEZING POINT.

variations in shrinkage distribution illustrated in Fig. 15. The 20 per cent cupronickel and both of the simple copper-nickel-zinc alloys piped internally, revealing large shrinkage cavities. The addition of either 4 per cent of tin or 5 per cent of lead to 20 per cent cupronickel functioned to transfer the shrinkage to the outside of the casting. In the 20 per cent

nickel, 6 per cent zinc alloy, which shows an internal shrinkage cavity similar to that of the cupronickel, neither 2 per cent of tin nor 2.5 per cent of lead was sufficient to completely transfer the shrinkage to the outside, although the internal cavity was diminished in each case; however, the simultaneous introduction of tin and lead in these amounts accomplished this result. As shown in the photograph, the simultaneous addition of 4 per cent of tin and 5 per cent of lead caused both the 6 per cent and 15 per cent zinc alloys to pipe externally.

It appears probable that the manner of distribution of the freezing shrinkage is more important than its extent, within the range of alloys studied. Normally, it would seem preferable to use an alloy that is able to feed itself in such a fashion as to collapse on the shrinkage void, resulting in a slight distortion of the casting rather than in unsoundness. This is therefore an important function of tin and lead in the casting alloys.

Where a uniform temperature gradient and freedom from feeding difficulties exist, as in the production of ingot for subsequent rolling or extruding operations, the problem of shrinkage does not offer any serious obstacles.

TABLE 3.—*Comparison of Shrinkages*

Alloy	Composition, Per Cent					Contraction, In. per Ft.	Pattern- maker's Allowance, In. per Ft.
	Cu	Ni	Zn	Sn	Pb		
Nickel silver	bal.	20	6			0.17	$\frac{3}{16}$
	bal.	20	6	4		0.14	$\frac{3}{16}$
	bal.	20	6	4	5	0.14	$\frac{3}{16}$
	bal.	20	15			0.17	$\frac{3}{16}$
	bal.	20	15	4	5	0.13	$\frac{1}{8}$
	bal.	20	40			0.14	$\frac{3}{16}$
	bal.	20	12	4	10	0.16	$\frac{3}{16}$
	bal.	20	20	4	10	0.16	$\frac{3}{16}$
Red brass	85		5	5	5	0.16	$\frac{3}{16}$

*Patternmaker's Allowance for Shrinkage.*—The patternmaker's allowance for shrinkage to compensate for contraction in volume of a casting occurring after solidification, in cooling to room temperature, has been obtained for a number of alloys. The pattern used consisted of a  $1\frac{1}{4}$ -in. square bar, 14 in. long with a set of knife edges set 12 in. apart on each side of the bar, and was molded in green sand. The shrinkage, in inches per foot, was obtained by subtracting from 12 in. the measured distance between the knife edges on the casting. The values obtained are listed in Table 3.

It is apparent that even with considerable ranges in composition the same patternmaker's allowance may be used as for red brass; some foundries casting considerable amounts of both red brass and nickel silver use the same patterns for both, but with two sets of detachable gates and risers.

#### EFFECT OF DEOXIDATION PROCEDURE ON SOUNDNESS

A number of factors enter into the production of castings of commercial shapes, which are not involved in the production of well designed and easily fed tensile-test castings or ingots for subsequent rolling or extrusion. These involve the presence of gases evolved from the core, stresses set up in the casting by contraction of the solidifying metal about the core,

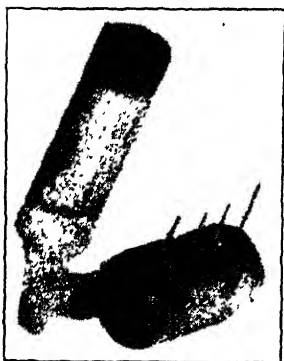


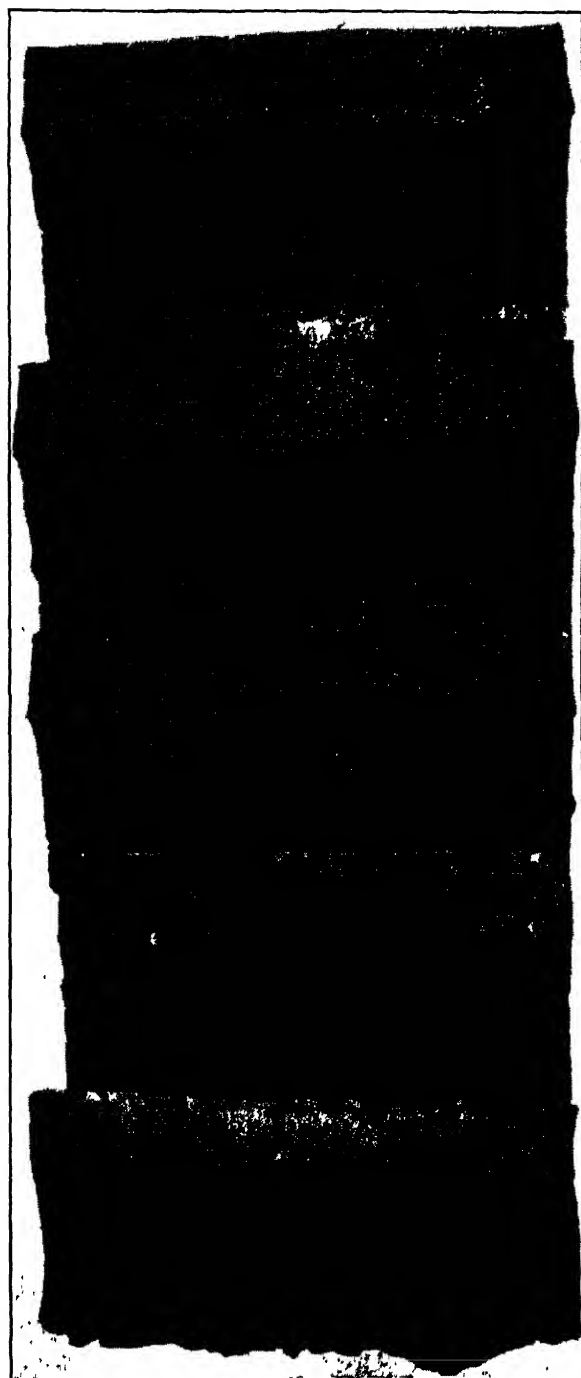
FIG. 16.—CASTING USED FOR HYDRAULIC AND FRACTURE TESTS.

turbulence and reuniting of metal streams, nonuniformity of section of castings, which introduce feeding difficulties and numerous other complications. Thus, while a melting procedure that gives good castings in commercial shapes will also give sound tensile bars, it does not necessarily follow that the converse is true.

The use of a test casting that to some extent at least involves the factors entering into the production of commercial castings is therefore more apt to develop information directly applicable to foundry practice than is the use of well fed tensile castings.

*Hydraulic and Fracture Tests.*—Fig. 16 shows the type of casting used to develop the effect of variations in deoxidation treatment on the soundness of the casting, and consists of a horizontally cast bushing 4 in. long by  $2\frac{3}{4}$  in. outside diameter with a  $\frac{3}{8}$ -in. wall. The alloy conforming to the desired composition for the Federal Specification WWP-541 (20 Ni, 4 Sn, 6 Zn, 5 Pb, bal. Cu) was used throughout. After being subjected to hydraulic tests, the cylinders were fractured longitudinally in four places; along the parting line at and opposite the gate, in the top of the cope and at the bottom of the drag. Hydraulic tests on castings poured at about  $2400^{\circ}$  F. are summarized in Table 4. Only the melts treated with 0.05 per cent Mg and with 0.05 per cent Mg + 0.10 per cent Mn were pressure-tight, despite the fact that all of the melts were quiet in the crucible and the metal froze quietly in the molds, the sprues showing good "pipes."

Hydraulic tests are subject to definite limitations, because leaks will occur only when the testing fluid can find a continuous, though tortuous, channel through the wall of the casting, and when used alone require



SHOWING EFFECT OF  
Proper Deoxidation  
with 0.10 per cent Mn  
0.05 per cent Mg

Proper Deoxidation  
with 0.10 per cent Mn  
0.05 per cent Mg  
0.02 per cent P

Addition of  
0.05 per cent B

Addition of  
0.30 per cent Si

Excessive Manganese  
0.25 per cent Mn  
0.05 per cent Mg

FIG. 17.—EFFECT OF VARIOUS DEOXIDIZERS ON FRACTURES OF NICKEL SILVER BUSHINGS.

statistical data from a large number of tests in order to detect rather small improvements in casting technique. However, hydraulic tests, in

TABLE 4.—*Hydraulic Tests on Castings Poured at About 2400° F.*

No	Deoxidizer, Per Cent	Water Pressure, Lb. per Sq. In.	
		40	1000
1	0.10 Si	S <sup>a</sup>	S
2	0.30 Si	L	LB
3	0.05 Li	S	S
4	0.05 B	S	S
5	0.10 Ti, 0.25 Mn	S	L
6	0.25 Mn	S	L
7	0.05 Mg	OK	OK
8	0.05 Mg + 0.10 Mn	OK	OK

<sup>a</sup> S, sweated; L, leaked; LB, leaked badly; OK, did not leak.

conjunction with observations of the fractures of castings made under a variety of controlled conditions of melting and deoxidation, have proved useful and permit a rapid method of estimating the soundness of the cast metal.

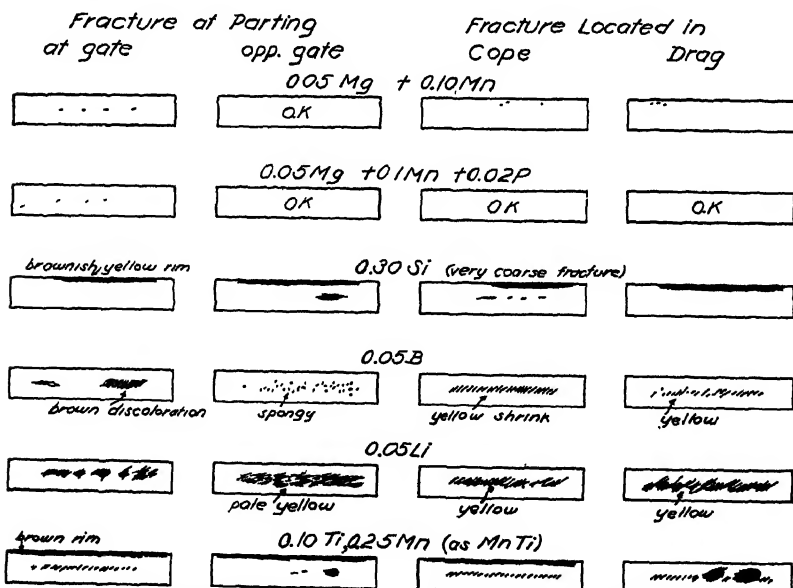


FIG. 18.—APPEARANCE OF FRACTURES IN ALLOY 20 PER CENT NI, 4 SN, 6 ZN, 5 PB, BALANCE CU.

Fig. 17 shows fractures of bushings made from metal in which some of the deoxidizers mentioned in Table 4 had been used. In Fig. 18 an

attempt has been made to express schematically the appearance of the fractures.

The detrimental effect of silicon upon alloys of the red brass type has been referred to frequently by foundrymen, its presence being considered unfavorable to pressure-tightness. It appears that silicon in amounts as small as 0.10 per cent is also highly objectionable in nickel silvers containing lead, the castings leaking in hydraulic tests. The surfaces of castings treated with silicon exhibit a peculiar lacy network, pronounced with 0.30 per cent silicon and noticeable with 0.10 per cent, which seems

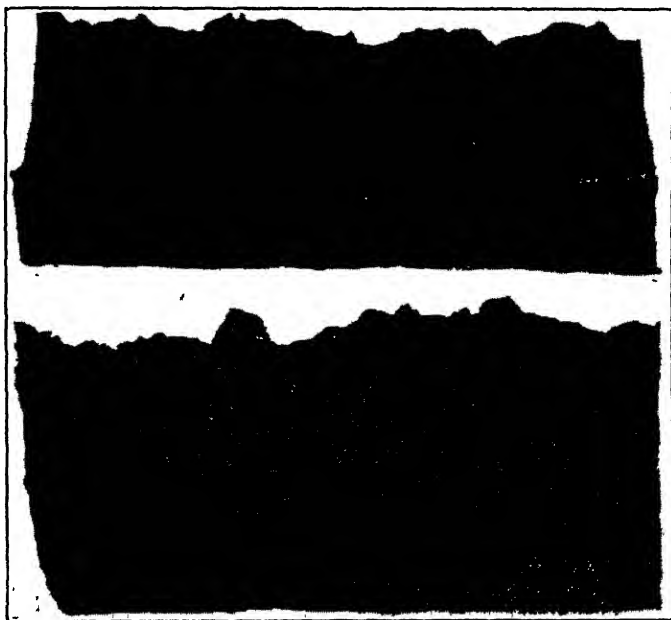


FIG. 19.—EFFECT OF 0.30 PER CENT SI ON FEDERAL SPECIFICATION ALLOY (20 NI, 4 SN, 6 ZN, 5 PB).

to be a focal point for “hot cracks,” while the fractures are invariably coarse grained. The surface effect and the coarse structure produced by silicon are apparent in Fig. 19.

Figs. 17 and 18 also show that the addition of such highly reactive elements as lithium, boron and titanium produced poor fractures, with spongy and discolored areas, despite the fact that the molten metal was quiet in the crucible and the mold, and froze quietly, the sprues showing no indication of gas evolution. Inasmuch as there was considerable slagging of the crucible with these elements, it was thought possible that some silicon was being reduced from the crucible. The lithium-treated melt was analyzed for silicon, a value of 0.02 per cent being obtained. Comparison with a melt treated with magnesium + manganese, which analyzed 0.004 per cent silicon, indicates the probability of about five



times as much "pick-up" of silicon in the former. Highly reactive elements such as lithium, when added in amounts sufficient to leave merely a trace after combining with the oxygen present, might prove useful, but in practice such a balance is not easy to maintain. Further, with charges composed partly of remelt gates and risers, the repeated use of such deoxidizers may ultimately cause an accumulation of an undesirable amount of silicon.

*Satisfactory Deoxidation Procedure.*—Since the use of magnesium with manganese gave consistently pressure-tight bushings and rather good fractures, a number of tests were made to develop the optimum amounts.

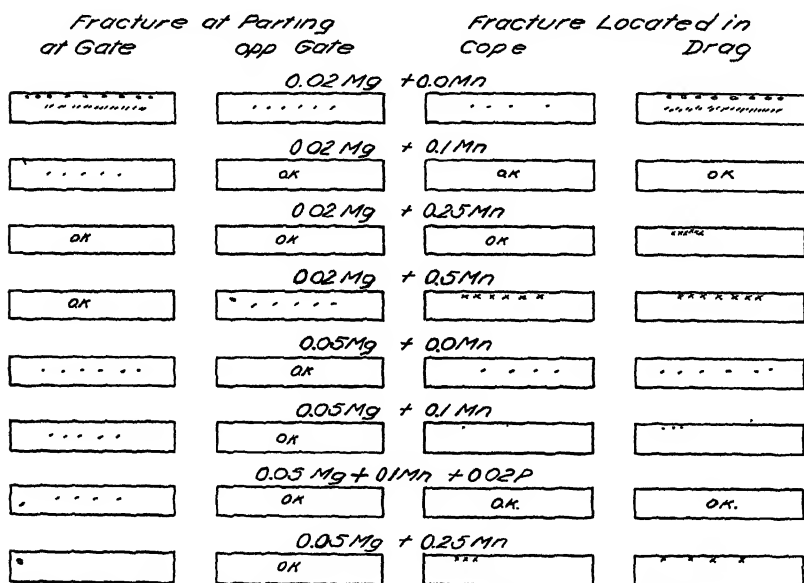


FIG. 20.—APPEARANCE OF FRACTURES IN ALLOY 20 PER CENT NI, 4 SN, 6 ZN, 5 PB, BALANCE CU.

The results of fracture tests are shown in Fig. 20. While 0.05 per cent magnesium used alone works rather well, 0.02 per cent is inadequate. The addition of 0.10 per cent manganese, added a few minutes before the magnesium, is helpful, but, as may be observed, when manganese reaches 0.25 per cent, there is a tendency for "dirt" or dark inclusions to appear in the fracture a little below the surface, an effect that is exaggerated with the addition of 0.50 per cent manganese. Therefore an excess of manganese should be avoided. The use of 0.02 per cent phosphorus added just before pouring is effective in clearing the surface of the melt and permitting more efficient skimming. An excess of phosphorus (0.05 per cent) is undesirable because it affects the ductility adversely.

At present the most satisfactory "deoxidation" treatment to produce pressure-tight castings in the 20 Ni, 4 Sn, 6 Zn, 5 Pb, bal. Cu type of alloy is that outlined in Table 5.

In making melts in crucible pits, the manganese is dropped into the crucible while it is in the furnace pit. The magnesium is added immediately after the pot is pulled (thus insuring a sufficient lapse of time before pouring), plunged to the bottom of the pot and stirred in well. The phosphor copper may be added after the crucible is taken over to the molds.

TABLE 5.—*Most Satisfactory Deoxidation Procedure*

Deoxidizer, Per Cent	Source	Time of Addition
0.10 Mn	97 per cent manganese metal	5-7 minutes before pouring
0.05 Mg	Magnesium (sticks)	3-5 minutes before pouring
0.02 P	15 per cent phosphor copper	Added just before pouring

While this procedure probably is open to improvement, it works well and has been found to give good castings from 150-lb. melts made from virgin metals in the oil-fired crucible pit type of furnace. When prepared ingot is used, or when a considerable portion of the charge consists of remelt, the procedure may be modified; for example, the use of manganese may be unnecessary. Melting equipment and conditions vary greatly from foundry to foundry and some experimentation as to the optimum amounts of deoxidizer may be necessary. It is hoped that this survey, however, will offer guidance to the foundryman in arriving at the best procedure for his particular conditions of melting.

*Deoxidation vs. Tensile Properties.*—Using the same alloy as in the fracture and hydraulic tests (20 Ni, 4 Sn, 6 Zn and 5 Pb, bal. Cu) the effect of variations in deoxidation procedure on tensile properties was ascertained with moderate additions of the following elements:

Silicon	Barium
Silicon + magnesium	Aluminum
+ boron	Calcium
+ calcium	Manganese
+ calcium + magnesium (added as copper-base alloy)	Magnesium + manganese
	Magnesium + manganese + phosphorus
Manganese + phosphorus	

All the melts were made in a 30-lb. high-frequency induction furnace, using an unlined clay-graphite crucible, and were cast at about 2450° F. into green sand. The type of tensile test casting is shown in Fig. 21. The tensile test results are summarized in Fig. 22. Generally, the results have been arranged in order of descending tensile strengths and the quantities in which the additions were made are indicated at the top of the figure. It has not been feasible to determine the optimum amounts for each "deoxidizer," and it is conceivable that some of the additions that

seem ineffective or undesirable may be useful in larger or smaller amounts than those employed in these tests.

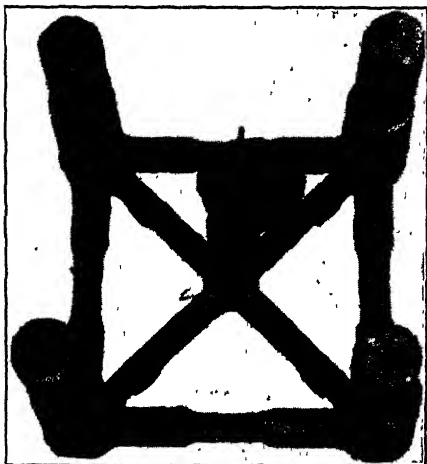


FIG. 21.—TENSILE-TEST CASTING.

that must be hydraulically tight, gave excellent tensile properties when used alone and in combination with magnesium, calcium or

In column 7 of Fig. 22 the tensile results obtained on deoxidation of the melt with Mg-Mn-P in the amounts found to be best for obtaining pressure-tightness are indicated, from which it may be seen that the following properties are secured: tensile strength, 45,000 lb. per sq. in.; yield point, 27,000 lb. per sq. in.; elongation, 15 per cent; hardness, 90 Brinell.

It may also be noted that silicon, which has been found decidedly detrimental in castings

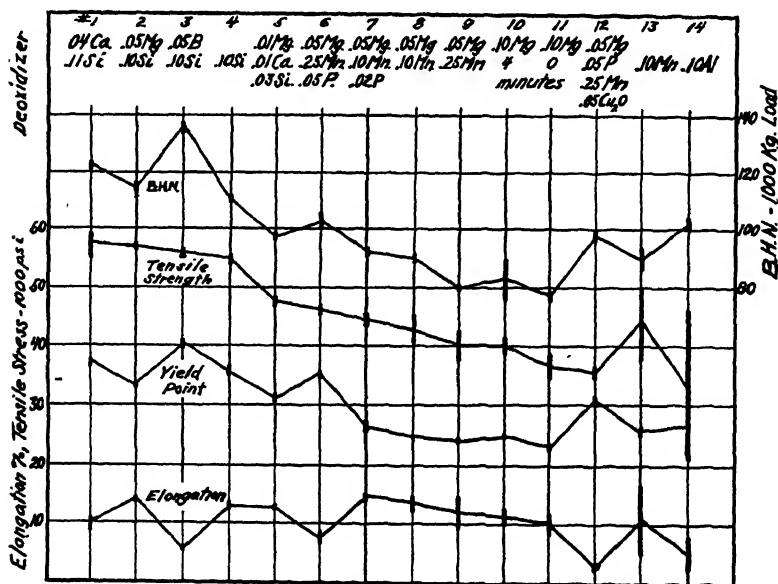


FIG. 22.—EFFECT OF VARIATIONS IN DEOXIDATION PROCEDURE ON TENSILE PROPERTIES OF FEDERAL SPECIFICATION ALLOY (20 NI, 4 SN, 6 ZN, 5 PB).

boron. However, the tensile specimen fractures of the silicon-treated melts, Nos. 1 to 4 inclusive, though clean and uniform, were rather coarse grained. The Brinell hardness curve explains in some measure the

higher strength properties of these melts. The tensile specimens from all of the melts treated with 0.10 per cent or more of silicon had hardnesses of 110 Brinell or more. In contrast, the tensile specimens from the melts treated with 0.05 Mg + 0.10 Mn + 0.02 P showed a Brinell hardness number of about 90. This difference of 20 Brinell may be due to a precipitation of an excess constituent, probably a silicide, in the silicon-treated melts. In view of its apparent tendency to render this alloy susceptible to hot tears, the use of silicon as a deoxidizer should not be recommended, particularly where pressure-tightness is required.

Too much phosphorus (column 6) apparently is undesirable, the elongation dropping rather sharply; this element should probably be kept below 0.025 per cent. Apparently even as highly reactive an element as magnesium requires a few minutes to function properly, as may be inferred from a comparison of columns 10 and 11. Aluminum and manganese added separately gave erratic responses, showing wide variations in properties in the same casting. The addition of 0.10 per cent barium, 0.10 per cent calcium, and of 0.25 per cent manganese + 0.05 per cent phosphorus was ineffective, the bars being too unsound to be machined.

#### TENSILE PROPERTIES OF FEDERAL SPECIFICATION 20 PER CENT [NICKEL SILVER AND RELATED ALLOYS

In the Federal Specification WWP-541, a minimum of 2.5 per cent tin and maxima of 10 per cent zinc and 6 per cent lead are permissible. The results of such variations on the tensile properties are shown in Fig. 23. These alloys were all deoxidized with 0.10 per cent silicon + 0.05 per cent magnesium; the strength properties therefore are somewhat higher than if the melts had been treated with Mg-Mn-P in the amounts desirable to insure pressure-tightness. However, these tensile tests permit a useful comparison of the alloys with each other, and indicate the trend and magnitude of the change in strength properties with composition.

*Effect of Zinc.*—The first set of curves shows that an increase in zinc from 6 to 10 per cent is accompanied by a moderate improvement in properties. It may be considered that variations of zinc within the specification limits will have a negligible effect on the strength properties, although the alloys higher in zinc may be less sensitive to gas troubles.

*Effect of Tin.*—In contrast to zinc, variations in tin affect the tensile properties markedly, as might be expected. This may be noted from the second set of curves, which show that lowering the tin to the 2.5 per cent minimum specified causes a sharp drop in hardness and tensile properties along with a marked increase in elongation. The properties of the 0 per cent tin alloy were also determined, although this tin-free alloy is outside the specification limits. A further drop occurred in strength properties, and the elongation also dropped. The casting made with the 0-tin alloy exhibited lead sweat, which seldom is evident in this type of

alloy when tin is present in amounts of 2.5 to 4 per cent. On one other occasion lead sweat was noticed in this type of alloy, also in the absence of tin, with an alloy containing 2 per cent of iron, in addition to 20 per cent nickel, 6 per cent zinc, and 5 per cent lead.

*Effect of Lead.*—Since no minimum is specified for lead, the effect of 0, 2.5 and 5 per cent was determined. From Fig. 23 it is apparent that the first addition of 2.5 per cent drops the elongation and the tensile strength, while increasing the lead from 2.5 to 5 per cent has less effect.

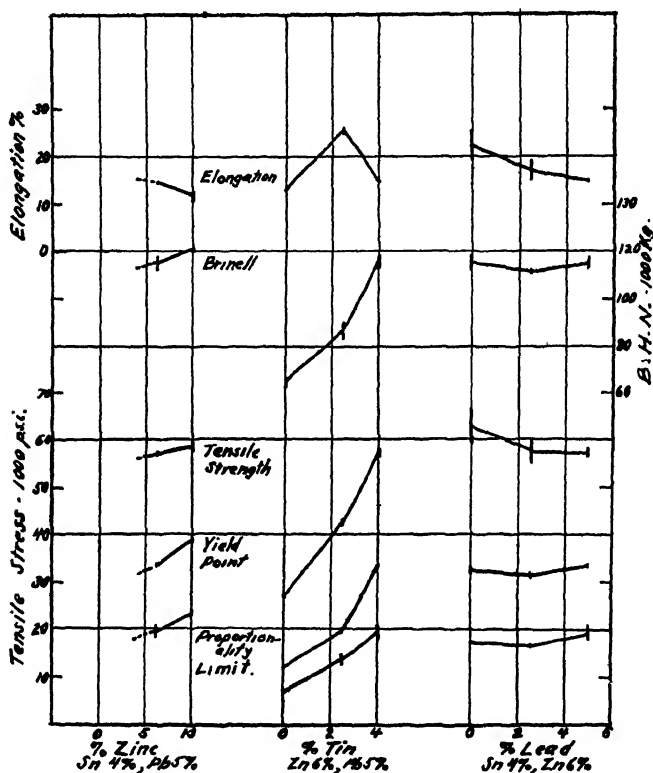


FIG. 23.—TENSILE PROPERTIES OF CAST FEDERAL SPECIFICATION ALLOY (20 PER CENT Ni) AND RELATED ALLOYS,

*Effect of Iron.*—Inasmuch as 1 per cent of iron (plus other impurities) is permissible, the effect was studied of 0.5, 1 and 2 per cent of this element on the physical properties. It was found that 1 per cent of iron could be tolerated, although no beneficial effects were obtained; 2 per cent of iron leading to segregation of iron, and, as a result, strength and ductility are deleterious. There seems to be no advantage to be gained in having iron present and it should be considered as an impurity to be kept as low as is practicable.

## ACKNOWLEDGMENTS

The authors acknowledge with pleasure the support and stimulation received from Messrs. A. J. Wadhams and P. D. Merica, executive officers of The International Nickel Company.

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## DISCUSSION

(W. P. Sykes presiding)

E. R. DARBY,\* Detroit, Mich.—What are the major foundry difficulties encountered in the handling of nickel silver?

T. E. KIHLGREN.—One of the difficulties that is normally encountered in the foundry, especially a foundry accustomed to producing brass castings, is that of obtaining a suitably high pouring temperature. A good many makers of brass castings are not accustomed to pouring castings with metal temperatures up to 2500°, and may find some difficulty in observing that requirement. Another difficulty, which should not trouble anyone who has been casting high-nickel alloys, is that of providing suitable means for adequately feeding the casting. Nickel silver casting alloys require much more generous provision for that than do the normal brass cast-

\* Metallurgist, Federal Mogul Corporation.

ings. In general, gates and risers three times as heavy as for red brass should be employed. Other precautions include the generous venting of the mold and the use of a reasonably open sand. Probably the two factors that cause most trouble are failure to use a high enough pouring temperature, and to mold as for a brass casting.

W. M. CORSE,\* Washington, D. C.—Those of us who have been working in this field for a number of years know how difficult it is to solve some of the foundry problems, and this paper will be of assistance. Manufacturers that advocate the use of nickel silvers, particularly those working to establish Federal Specifications for these alloys, are aware of the value of this product. If the foundry difficulties can be overcome, the use of solid nickel silver will be markedly extended.

These difficulties are very genuine, as those who travel about the country and talk with people who want to make nickel silver can testify. Several manufacturers have told me that they know solid nickel silver alloy is the best material for certain long-time installations, that they want to make it, but cannot afford to do so because of the foundry difficulties and the high percentage of loss. If such losses can be held down to a figure approximating those on red brass, the rest of the problem will be comparatively easy.

Selling solid nickel silver fixtures instead of red brass plated fixtures is on a parallel with selling sterling silver instead of silver plate. No difficulty is encountered in selling the sterling article, if the buyer can afford to pay the price. Solid metal is superior to plated, particularly in plumbing fixtures, as anybody who has had experience with plated equipment can testify. No matter what the location, the plate will wear off if the fixtures are subjected to much wear and cleaning, and replacements are expensive.

Solid nickel silver plumbing fixtures and fittings are being more and more used, particularly in monumental buildings where long life must be considered, and where cleaning and replacement costs must be kept at a minimum; 20 per cent solid nickel silver plumbing fixtures have been used in practically all of the Government buildings in the recent monumental building project, particularly where the cost of the building exceeds one million dollars. These solid white-metal installations are chromium-plated for the most part, to keep cleaning costs down, as chromium-plated articles can be washed off and kept looking bright with less effort than is required with unplated white-metal fixtures.

An example of the long life and excellent service given by solid white metal with 20 per cent nickel content is offered in the old part of the Senate office building, where such fixtures have been in use for more than 25 years. The installation was made by Meyer & Sniffen when the building was erected. The fixtures have had only ordinary attention and cleaning and they look practically new today.

It would seem that a material that is valuable from a decorative standpoint as well as a utilitarian one is worth working with in order to eliminate the foundry difficulties, and I believe that the authors of this paper have contributed a great deal to helping the foundryman.

E. FETZ,† New York, N. Y.—The authors must be complimented on the wealth of data presented in their paper. Emphasis has been placed on two important properties of Cu-Ni-Zn alloys; viz., color and hardness. Whereas the hardness of the sand-cast alloys containing 0 to 10 per cent Pb (Fig. 7) shows a behavior one would reasonably expect, there are anomalies in the 2 to 8 per cent tin-bearing alloys, according to Fig. 6, which deserve some further interpretation. Contrary to the authors' statement (p. 291), Fig. 6 proves that an addition of 2 per cent Sn reduces

\* Consulting Metallurgist.

† Special Student, X-Ray Department, School of Mines, Columbia University.

the hardness of the high-nickel high-zinc region to a maximum extent of about 60 Brinell. Two years ago, Heike, Schramm and Vaupel established that the solubility of zinc in nickel does not remain constant with falling temperatures, but drops from 43 per cent Zn to 33 per cent Zn. It is not difficult to draw up provisionally the alpha solid solution space of the ternary Cu-Ni-Zn diagram. Taking Figs. 6 and 7 into account, one must conclude that the abrupt gain in hardness in the free-tin, high-nickel, high-zinc alloys is attributable to precipitation-hardening effects in the sand mold. The second case of "abnormal" hardness change occurs in the 8 per cent Sn alloys that are high in nickel and low in zinc (Fig. 6d). Here the hardening effect of tin exceeds that which one would expect in a solid solution of Cu-Ni (-Zn). The abrupt hardness change can either be due to the appearance of a new constituent, as, for instance, the effect of  $\text{Cu}_3\text{Sn}_5$  in tin bronzes, or to appreciable aging effects. The Brinell hardness of 205 units in the 8 Sn, 2.5 Zn and 25 Ni alloy (according to Fig. 6d) seems to indicate that the latter assumption holds true. Owing to the low zinc content, the ternary Cu-Ni-Sn diagram can be intelligently consulted. Mr. Wise previously introduced before this Institute the  $300^\circ\text{C}$ . isotherm which, however, could not be verified by my own investigations in the alloy range under discussion. The revised alpha solid solution space, the hardness of these alloys in the annealed, sand-cast and fully aged state, will be published soon and will quantitatively show the remarkable extent of precipitation-hardening. Since the hardness of sand-cast, age-hardenable alloys greatly depends on the cooling speed in the sand mold utilized and even on the section of the casting where the hardness has been measured, it appears that sand-casting hardness charts furnish too arbitrary a basis for comparison. In addition to this, variations of the chemical analysis considerably shift the homogeneity range of the alpha phase in regard to concentration and temperature (as is clearly shown by the addition of 2 per cent Sn according to Fig. 6b) so that the iso-hardness curves of the sand-cast state could not be consulted. Since the ternary, quaternary (and higher) constitutional diagrams have not yet been established so that sound predictions could be made as to the nature of sudden hardness changes, the annealed condition as a reference would eliminate the question of precipitation-hardening. It appears advisable to replace or at least to supplement iso-hardness charts derived from sand-cast alloys (Fig. 6) by charts obtained on annealed specimens. This method would also have the advantage of permitting definite conclusions regarding the machinability of an alloy and the possibilities of thermal treatments. Remarkable color changes accompany the breakdown of solid solutions in the copper corner of Fig. 6d. These alloys exhibit a silvery white luster in the annealed state but turn decidedly red when reaching the thermodynamic equilibrium state in the range of heterogeneity. This phenomenon must certainly be attributed to the following facts: Nickel exerts a strong coloring effect on copper-rich alloys, presumably it is uniformly distributed in solid solution. Owing to the precipitation of a nickel-rich phase, the parent solution becomes impoverished in nickel and the heterogeneous alloy undergoes a distinct color change. Although most pronounced in age-hardening copper-rich alloys of a "critical" nickel content, color deviations from the homogenized state have been observed on sand-cast alloys of which the constitutional diagrams show a wide gap between the solidus and liquidus. Since the state of heterogeneity of sand-cast alloys does not represent a well defined thermodynamic state, color determinations referring to annealed samples would offer the safest basis for comparative measurements. Naturally this precaution is rendered superfluous in connection with alloys in which the strong coloring effect of high nickel contents predominates at all events. Unfortunately, the authors did not find photometric measurements very useful. Since the human eye admittedly shows deficiencies in the determination of slight color variations, it would mean a great step forward to place color determinations on a scientific basis, which can be quantitatively checked by



instruments and which would allow comparisons with alloys not included in this paper. Photometric analysis of the entire spectrum reflected from metallic surfaces has been attempted abroad with fair success. In view of the meager literature on Cu-Ni-Zn alloys, the present paper offers valuable information in this field.

T. E. KIRLGREN, N. B. PILLING AND E. M. WISE.—Since the primary object of our work was the study of cast nickel silvers, which are normally employed in the as-cast state and are thus clearly not in equilibrium, a discussion of the possible behavior of these materials when in equilibrium at particular temperatures would not be of direct value. In this connection, we might, however, refer to the work of Bauer and Hansen on the Influence of Nickel on the Constitution of Copper Zinc Alloys [*Ztsch. f. Metallkunde* (1929) 21, 357]. This distinction with respect to state is important and should be recognized. In extrusion alloys, the shape and location of the  $\alpha$ ,  $\alpha + \beta$ , and  $\beta$  fields are of course important and have received adequate attention by those producing such products.

The general influence of tin is, as stated, to harden the alloys, although appreciable increases in hardness are not obtained until the tin contents are in excess of 2 per cent. Fig. 6 shows that for alloys containing up to 30 per cent Ni and up to 30 per cent Zn, the effect of 2 per cent Sn is mild, although usually positive, and further additions of tin result throughout most of the range in quite substantial increases in hardness. It will be noted that no attempt has been made to carry the iso-hardness curves of Figs. 6b, c and d up to 40 per cent Zn, since the data for the complex alloys in this region are based on alloys containing 0 to 30 per cent Zn. Obviously, this area is considerably beyond the range in which the tin-content nickel silvers would find employment for casting purposes. In 6a, alloys containing up to 50 per cent zinc were available, making it possible to show the iso-hardness curves over a wider range than was possible for the quaternary and five component alloys.

The nickel bronzes have been reported on in detail in papers by several investigators, including Price, Grant and Phillips, Eash and Upthegrove, and Wise and Eash, all of which are accessible in the Institute *Transactions*, so that further discussion appears unnecessary at this time, especially so when no data are offered.

With regard to color estimation, and particularly to the establishment of the tolerable departure in color, the problem was essentially one in psychology rather than in physics in view of the fact that one of the important points at issue was the establishment of a visually acceptable match between wrought and cast alloys. As a post-mortem, colorimetric measurements might be interesting but the results are unlikely to be very appealing to the practical foundrymen. The difficulty in directly visualizing the color resulting from a particular wave-length-reflectivity contour can best be appreciated by examining existing data on copper, gold and some of the other metals. The trichromatic delineation of such data is perhaps more comprehensible but the difficulty of conversion is considerable. In this connection, reference might be made to a recent publication of the Bureau of Standards [Color and Spectral Transmittance of Vegetable Oils by H. J. McNicholas, *R.P.* 815 (1935)].

Some recent observations have been reported in Germany on the colors of the gold-palladium system utilizing a particular series of tricolor filters. The data indicate that the principal result of adding moderate amounts of palladium to gold is to lower the reflectivity for the red more rapidly than for the other two colors. Information of this type is not particularly helpful as a primary source of information to determine the necessary and attainable approximation between the colors of commercial alloys.

## Properties of the Platinum Metals

### I—STRENGTH AND ANNEALING CHARACTERISTICS OF PLATINUM, PALLADIUM, AND SEVERAL OF THEIR COMMERCIAL ALLOYS

BY E. M. WISE\* AND J. T. EASH,\* MEMBERS A.I.M.E.

(New York Meeting, February, 1935)

PLATINUM and palladium are the most generally useful, most ductile and least rare members of the platinum family. They have many important applications in the pure state but for other applications it is frequently desirable to harden them and otherwise modify their properties by alloying small amounts of the other platinum group metals with them. These alloys are frequently required to withstand very drastic forming operations and to possess certain mechanical properties to fulfill specific requirements. For these reasons a knowledge of the tensile properties and annealing characteristics of pure platinum and palladium as well as their more useful commercial alloys is important to the user and the fabricator. The present work was undertaken to fill this need. Rather brief (5 min.) annealing treatments were employed to render the data of maximum practical value and all tests were conducted upon 0.050-in. dia. wire, initially reduced 50 per cent in area by cold drawing, for the same reason.

### CONCLUSIONS

1. Pure (thermocouple grade) platinum reduced 50 per cent by cold drawing exhibits the following tensile properties: ultimate tensile strength, 36,000 lb. per sq. in.; proportional limit, 27,000 lb. per sq. in.; elongation, 2.5 per cent in 2 in.; reduction in area, 95 per cent. When fully annealed by treatment at 1100°C. its properties are: ultimate tensile strength, 20,700 lb. per sq. in.; elongation, 30 per cent in 2 in.; reduction in area, 93 per cent.

2. The addition of alloying elements in moderate amounts markedly increases the strength and annealing temperature without much detriment to the ductility.

The behavior and properties of variously hardened platinum alloys are considered in some detail. The behavior of a 20 per cent iridium

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\* Research Laboratory, The International Nickel Co., Bayonne, N. J.

platinum is typical and such an alloy reduced 50 per cent by cold drawing exhibits an ultimate strength of 140,500 lb. per sq. in., a proportional limit of 101,000 lb. per sq. in., elongation of 2.5 per cent in 2 in., and reduction of area of 85 per cent; and after a softening anneal at 1400°C. develops the following properties: ultimate tensile strength, 93,500 lb. per sq. in.; proportional limit, 59,100 lb. per sq. in.; elongation, 20 per cent in 2 in.; reduction of area, 88 per cent.

3. Commercially pure palladium reduced 50 per cent in area by cold drawing exhibits an ultimate of 46,900 lb. per sq. in.; proportional limit, 31,800 lb. per sq. in.; elongation, 1.5 per cent in 2 in.; reduction of area, 91.5 per cent; and after complete softening by annealing at 800°C. develops the following properties: ultimate, 30,400 lb. per sq. in.; elongation, 39 per cent in 2 in.; reduction of area, 91.5 per cent.

4. Palladium hardened by the addition of 4 per cent Ru, 1 per cent Rh, reduced 50 per cent in area by cold drawing, exhibits an ultimate of 71,500 lb. per sq. in., proportional limit of 46,300 lb. per sq. in., elongation of 3 per cent in 2 in. and a reduction of area of 84.5 per cent; and after annealing at 800°C., an ultimate of 55,200 lb. per sq. in.; proportional limit of 21,100 lb. per sq. in.; elongation, 25.5 per cent in 2 in.; reduction of area, 84 per cent.

5. The elongations of all wires increase to a maximum and then fall more or less slowly with a further increase in annealing temperature. In some instances this fall is due to marked selective grain growth. The reduction of area is high in all cases and shows only a small change as a result of the annealing treatments.

6. The effects of time and annealing atmosphere upon the properties of pure palladium have been determined.

7. The optimum annealing temperatures for a variety of platinum and palladium alloys are indicated, together with the properties before and after these treatments.

### PREVIOUS WORK

A considerable amount of information upon the constitution, hardness and electrical properties of the platinum metal alloys is scattered through the literature but the varying experimental conditions and in some cases the doubtful purity of the alloys, and the lack of systematic tensile data, make much of this work of rather limited value to the practical metallurgist. Much useful information concerning the hardness, physical and chemical properties of the platinum metals and certain of their alloys has been presented by F. E. Carter<sup>1</sup>, and in a later contribution<sup>2</sup> of this

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<sup>1</sup> F. E. Carter: The Platinum Metals and Their Alloy. *Trans. A.I.M.E.* (1928) **78**, 759-782.

<sup>2</sup> F. E. Carter: Platinum and Platinum Metals. *National Metals Handbook* (1933) 1365-1374.

worker the variation in hardness with annealing treatments has been concisely presented. A summary of information concerning the constitution and properties of a number of alloys of the platinum metals with elements outside the platinum group has been presented by Wise and Crowell<sup>2</sup>.

### PROCEDURE

The wires employed in this research were supplied by Baker & Co., and were produced on a commercial scale, and may be considered representative of commercially available materials of high quality. All wires were annealed at a diameter of 0.071 in. and then cold-drawn to a diameter of 0.050, making the final reduction of area 50 per cent.

TABLE 1.—*Compositions of Samples*

Metal or Alloy	Weight Per Cent					
	Pt	Pd	Ir	Rh	Ru	Ni
C.P. Pt.....	99.9+					
No. 1 Pt.....	99.9 <sup>a</sup>					
Ir-Pt.....	95. <sup>a</sup>		5 ± 0.1			
	90. <sup>a</sup>		10 ± 0.1			
	80. <sup>a</sup>		20 ± 0.1			
Rh-Pt, catalyst.....	90.			10		
Pd-Pt.....	75. <sup>a</sup>	20.		5		
Ni-Pt.....	95. <sup>a</sup>					4.5 - 5
No. 1 Com. Pd.....		99.9 <sup>a</sup>				
Rh-Ru-Pd, medium hard.....		95. <sup>a</sup>		3	2	
Rh-Ru-Pd, hard.....		95. <sup>a</sup>		1	4	

<sup>a</sup> Remainder of composition is principally the other platinum metals.

The type compositions of all samples is given in Table 1. The compositions were selected to embrace pure metals, the usual jewelry, electrical and dental grades of iridium platinum, the 10 per cent rhodium-platinum alloy used for ammonia oxidation and for electric furnace windings and in a closely standardized grade for thermocouples. The 5 per cent nickel-platinum alloy was included because of its importance as a filament material in the long-life amplifying tubes used in telephony. The No. 1 palladium is the material widely employed for electrical contacts while the two rhodium-ruthenium-palladium alloys are primarily employed for jewelry.

<sup>2</sup> E. M. Wise and W. S. Crowell: The Role of the Platinum Metals in Dental Alloys. *Trans. A.I.M.E.* (1932) 99, 365-383.

Annealing treatments were conducted in an electric furnace in an air atmosphere with the exception of those at 1100° and 1200°C., which were carried out in a gas furnace. The wire samples were introduced into the furnace together with a small thermocouple, and the annealing time was 5 min. at temperature, except where otherwise noted. The tensile tests were conducted on a small Amsler machine and specimens possessing a 2-in. gage length were employed in all cases. An Anderson

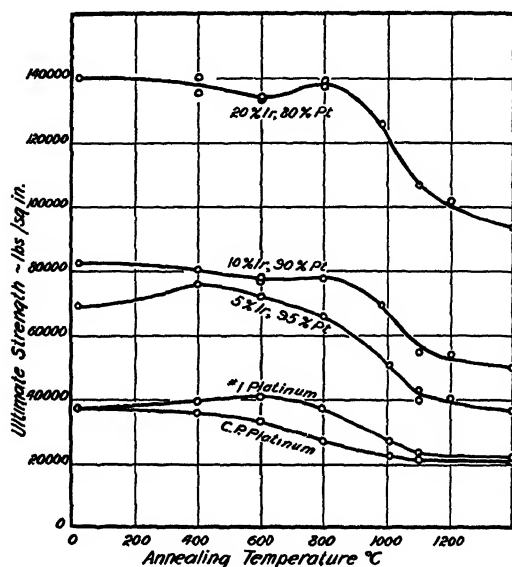


FIG. 1.—ULTIMATE STRENGTH VS. ANNEALING TEMPERATURE OF PLATINUM AND IRIDIUM-PLATINUM ALLOYS.

extensometer was utilized in determining the elastic properties. The reduction of area was determined by optical measurements of the fractured specimens.

## RESULTS

The effect of annealing temperature upon the ultimate strength of pure (thermocouple grade) platinum, No. 1 platinum and the 5, 10 and 20 per cent iridium-platinum alloys is shown in Fig. 1. The influence of the alloying additions upon the strength and annealing temperature is clearly evident. Corresponding curves showing the variation in proportional limit with the annealing temperature are shown in Fig. 2. The proportional limit of 20 per cent iridium-platinum alloy exhibits a marked hiatus from 400° to 800°C., perhaps arising from slight precipitation effects. The influence of the annealing treatment upon the elongation is presented in Fig. 3. The elongation of pure platinum rises to a

rather sharp maximum followed by a slower fall. A similar behavior but at higher temperature is shown by the platinum alloys. With the iridium-platinum alloys, additional points were obtained at tem-

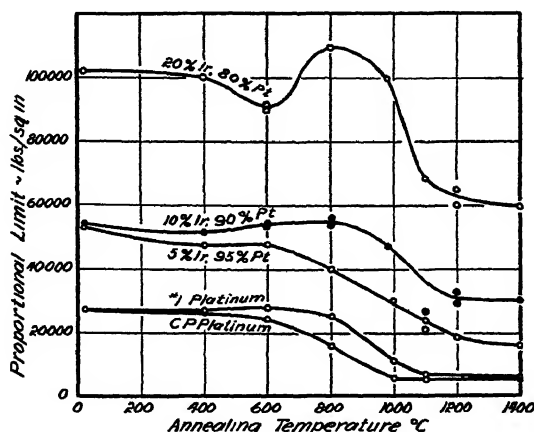


FIG. 2.—PROPORTIONAL LIMIT VS. ANNEALING TEMPERATURE OF PLATINUM AND IRIIDIUM-PLATINUM ALLOYS.

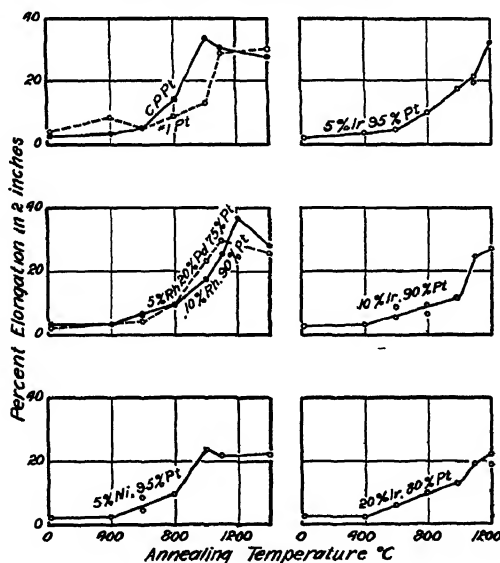


FIG. 3.—ELONGATION VS. ANNEALING TEMPERATURE OF PLATINUM AND PLATINUM ALLOYS.

peratures beyond the limits of the graph, which indicate that the values shown are not exceeded.

The relation between the annealing temperature and the reduction of area is shown in Fig. 4. The values are high throughout and surprisingly little change occurs except at the very high annealing temperatures.

Corresponding tensile data for the 5 per cent Ni-Pt, 5 per cent Rh, 20 per cent Pd, platinum and 10 per cent Rh-Pt alloys are presented

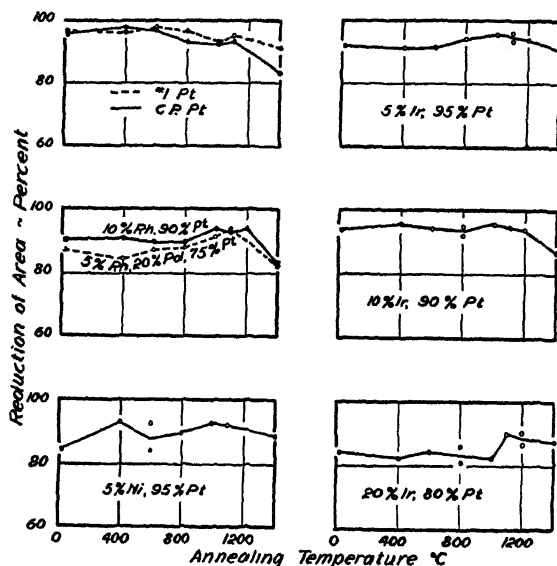


FIG. 4.—REDUCTION OF AREA VS. ANNEALING TEMPERATURE OF PLATINUM AND PLATINUM ALLOYS.

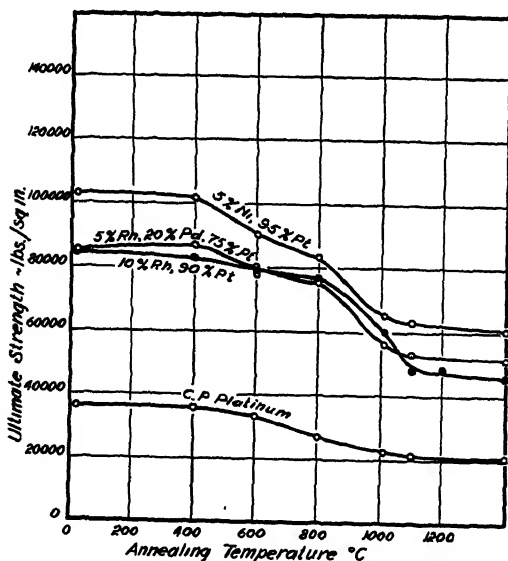


FIG. 5.—ULTIMATE STRENGTH VS. ANNEALING TEMPERATURE OF SPECIAL PLATINUM ALLOYS.

in Figs. 3, 4, 5 and 6 which require no special comment except that nickel appears to be a surprisingly effective hardener.

## PALLADIUM AND SOME OF ITS ALLOYS

The influence of the annealing temperature upon the tensile strength of commercial palladium and the 3 per cent Rh, 2 per cent Ru, and 1 per cent Rh, 4 per cent Ru, 95 per cent Pd alloys is shown in Fig. 7. The strength of palladium is higher than platinum in both the hard-drawn and annealed states, and becomes fully softened at a lower temperature.

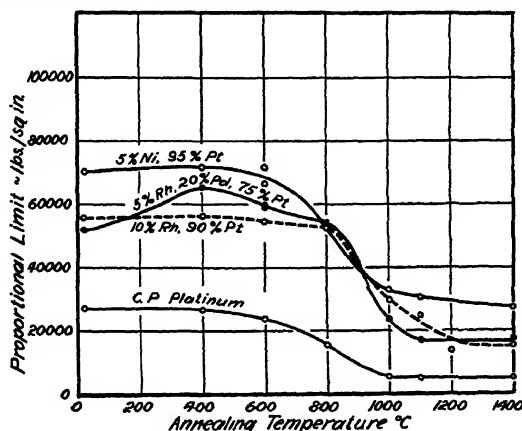


FIG. 6.—PROPORTIONAL LIMIT VS. ANNEALING TEMPERATURE OF SPECIAL PLATINUM ALLOYS.

Ruthenium appears to be quite effective in hardening palladium and at the same time increases the annealing temperature, but as will be observed later, it moderately but definitely reduces the reduction of area. The

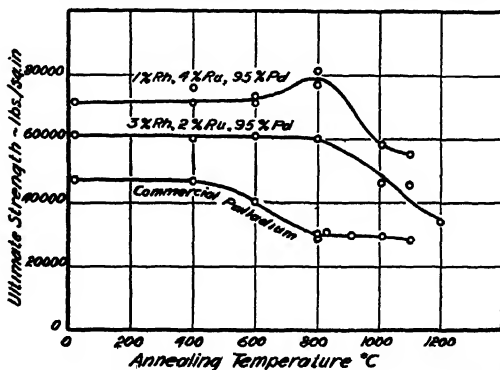


FIG. 7.—ULTIMATE STRENGTH VS. ANNEALING TEMPERATURE OF PALLADIUM AND PALLADIUM ALLOYS.

tensile strength temperature curve of the 4 per cent Ru 1 per cent Rh suffers a perturbation at about 800°C., analogous to that exhibited by the 20 per cent iridium-platinum alloy. This may be due to a mild precipitation-hardening reaction. The values of proportional limit vs. annealing temperature are presented in Fig. 8 and require no comment.



The curves for elongation vs. annealing temperature are presented in Fig. 9. It will be noted that a well defined maximum exists in the No. 1 palladium but that anneals above 1000°C. result in a pronounced fall in elongation. This is due to the onset of marked selective grain growth

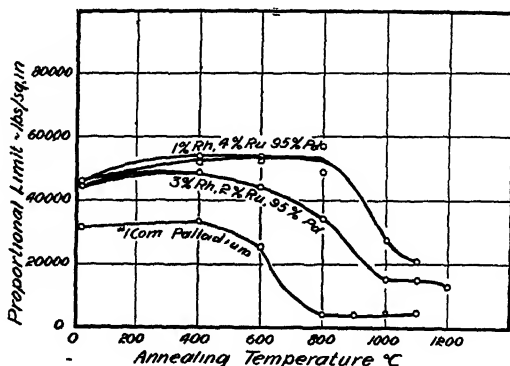


FIG. 8.—PROPORTIONAL LIMIT VS. ANNEALING TEMPERATURE OF PALLADIUM AND PALLADIUM ALLOYS.

giving rise to a very mixed grain size, as is evident from Fig. 10, which shows the appearance of the sample of No. 1 palladium annealed at 1100°C. At temperatures below this the grain size is very uniform, as shown in Fig. 11. The reason for this behavior has not been estab-

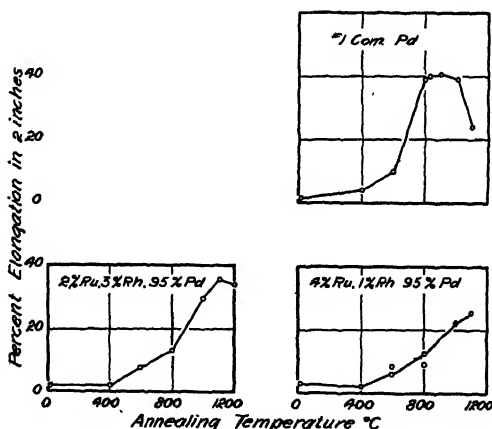


FIG. 9.—ELONGATION VS. ANNEALING TEMPERATURE OF PALLADIUM AND PALLADIUM ALLOYS.

lished, but undoubtedly it is due to the presence of a trace of grain growth obstructive material. The hardened palladiums do not show this marked drop in elongation.

The curves for reduction of area vs. annealing temperature are shown in Fig. 12 and, as with the platinum alloys, the values are high and surprisingly insensitive to the temperature of the anneal.

INFLUENCE OF TIME AND ATMOSPHERE UPON ANNEALING OF  
No. 1 PALLADIUM

It was found that increasing the time of anneal from 5 to 30 min. at an annealing temperature of  $830^{\circ}\text{C}$ . and in an air atmosphere resulted in a fall of less than 3 per cent in the ultimate strength and a negligible

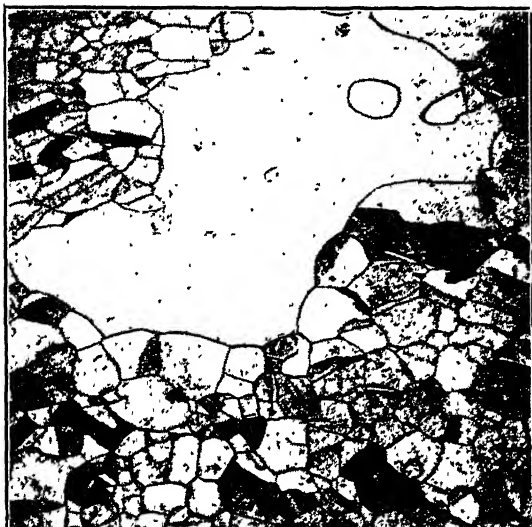


FIG. 10.—MICROSTRUCTURE OF No. 1 COMMERCIAL PALLADIUM ANNEALED 5 MIN. AT  $1100^{\circ}\text{C}$ .



FIG. 11.—SAME MATERIAL ANNEALED 5 MIN. AT  $830^{\circ}\text{C}$ .

Both samples etched with aqua regia.  $\times 100$ .

decrease (from 40 to 41 per cent to 38 per cent in 2 in.) in the elongation. Likewise the properties of palladium annealed for 30 min. in hydrogen and cooled in air were substantially the same as in samples annealed in air only. However, it was observed that samples annealed in hydrogen

and rapidly cooled in this gas were markedly harder and slightly less ductile than those annealed in air or in hydrogen and cooled in air. The tensile strength was raised from 30,000 to 48,000 lb. per sq. in. and the elongation was lowered from 38 per cent in 2 in. to 28 per cent. Samples annealed in nitrogen at 830° and 900°C. exhibited properties similar to those annealed in air but a nitrogen atmosphere may be useful in annealing very thin samples where the slight surface discoloration developed in air anneals is objected to. Further, it should be noted that a light surface checking became evident as a result of the tensile test in No. 1

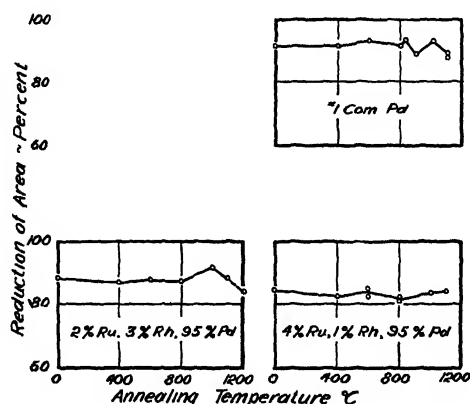


FIG. 12.—REDUCTION OF AREA VS. ANNEALING TEMPERATURE OF PALLADIUM AND PALLADIUM ALLOYS.

palladium wires annealed in air. This effect was not evident in the wires annealed in hydrogen, nitrogen or in vacuo and was very slight in the 3 per cent Rh, 2 per cent Ru alloy annealed in air. Samples of palladium annealed in vacuo at 1100° C. exhibited tensile properties substantially identical with those resulting from anneals in the gas furnace.

#### OPTIMUM ANNEALING TEMPERATURES FOR PLATINUM, PALLADIUM AND CERTAIN OF THEIR ALLOYS

An estimate was made of the optimum annealing temperatures for the several materials tested after a consideration of the tensile strength, elongation and surface appearance. The latter is indicative of the grain size, and considerable weight must be attached to it where appearance is a primary essential, as is frequently the case with these metals.

The properties of the alloys reduced 50 per cent by cold-drawing, and after the recommended anneals, are assembled in Table 2. It is believed that this information will be a useful guide in the selection and treatment of the more usual platinum-metal alloys. Obviously, where long anneals are employed slightly lower temperature can be used.

TABLE 2.—*Physical Properties of Platinum Metals and Alloys Cold-drawn (50 Per Cent Reduction) and after Recommended Anneals*

Material	Recommended 5-min. Anneal		Proportional Limit, Lb. per Sq. In.	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Reduction of Area, Per Cent
	Deg. C.	Deg. F.				
C.P. Pt.....	900-1000	1652-1832	27,000 10,000-5,300	36,000 24,000-22,000	2.5 24-34	95 92
No. 1 Pt. ....	1050-1100	1922-2012	27,000 8,500-6,500	36,700 25,000-23,000	3.5 21-29	96 94-95
5 per cent Ir, 95 per cent Pt	1100-1200	1922-2192	53,500 23,000-18,000	69,100 41,500-39,000	2.0 22-32	92 95-94
10 per cent Ir, 90 per cent Pt	1100-1200	1922-2192	54,000 36,000-30,000	82,200 55,000-53,000	2.5 25-27	94 95-94
20 per cent Ir, 80 per cent Pt	1200-1400	2192-2552	100,900 62,000-59,000	140,500 102,000-93,000	2.5 21-20	84.5 89-88
10 per cent Rh, 90 per cent Pt .....	1100-1200	1922-2192	55,600 22,000-17,000	84,300 49,000-47,000	3.0 25-37	90 93-94
5 per cent Rh, 20 per cent Pd, 75 per cent Pt.....	1000-1100	1652-2012	51,900 23,500-17,000	85,000 57,000-53,000	1.75 23-29	87 91-94
5 per cent Ni, 95 per cent Pt	1000	1652	70,000 33,000	103,100 65,000	2.0 23.5	84 93
No 1 Com. Pd... ..	800-900	1472-1652	31,800 5,000	46,900 30,000	1.5 39-41	91.5 92-89
3 per cent Rh, 2 per cent Ru, 95 per cent Pd. ....	1000-1100	1652-1922	46,050 16,000-15,500	61,000 46,000-41,000	2.0 30-36	88.5 92-88
1 per cent Rh, 4 per cent Ru, 95 per cent Pd .. ..	1000-1100	1652-1922	46,300 28,000-21,000	71,500 59,000-55,000	3.0 23-26	84.5 84

### DISCUSSION OF DATA

It is evident, from the data that have been presented, that a wide range of properties can be secured in generally available platinum and palladium alloys through the use of appropriate hardeners and annealing treatments, but it should be borne in mind that other special requirements frequently dominate in the final choice. Among these are ease of remelting and the constancy of composition despite repeated remelting, trade practices and the requirements of various stamping acts. Certain of the auxiliary elements likewise contribute certain desirable properties aside from their effect upon the tensile properties. Rhodium, for instance, is highly desirable in platinum used for ammonia oxidation

catalysts, for crucibles and high-temperature furnace windings, and for electrical contacts and, of course, for thermocouples. Iridium is highly desirable in platinum alloys for jewelry, because of the excellence of the alloys and because of established trade practices, and in electrical contacts that are required to operate under drastic conditions. Iridium and rhodium are likewise useful additions to platinum to be used for electrochemical operations involving the liberation of halogens. Palladium likewise is a very effective addition to platinum in electrical contact service. It may be noted in passing that high hardness in electrical contacts is generally not required and the useful effect of the alloying elements is largely due to factors other than their contribution to hardness. In the palladium alloys, rhodium appears to be a very desirable component in securing a brilliant polish, while ruthenium is primarily useful as a hardener. It may be noted that the higher rhodium, lower ruthenium alloys are best suited to deep draws, particularly in sections that are perforated prior to drawing and where trouble is to be expected from corner tearing.

#### ACKNOWLEDGMENTS

The authors wish to express their thanks to Messrs. A. J. Wadhams and P. D. Merica, executive officers of The International Nickel Company, for supporting this research and permitting its publication, and to Messrs. F. E. Carter and C. S. Sivil of Baker & Company for their cooperation in preparing the metals and alloys studied.

#### DISCUSSION

*(Eric R. Jette presiding)*

T. A. WRIGHT,\* New York, N.Y.—The authors say (p. 315), "The compositions were selected to embrace pure metals, the usual jewelry, electrical and dental grades of iridium-platinum . . ." I do not think they mean to imply that the usual or commercial grades are of the purity given here for the No. 1 or iridium-platinum, do they? That the impurities are so low? One-tenth?

J. T. EASH.—Yes, that was our understanding.

T. A. WRIGHT.—That is for the alloys you used. But you do not consider those typical of commercial jewelry alloy purity, do you; that is, of various makes in general?

J. T. EASH.—It would be impossible to vouch for the purity of all varieties of platinum that might be employed, which might contain miscellaneous secondary or incompletely refined metal and which may have been further contaminated by improper remelting. The materials tested are standard, readily available products and are believed to be as stated; namely, "representative of commercially available materials of high quality." In view of the fact that the bulk of the platinum is melted by the supplier indicated, the selection appears appropriate.

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\* Secretary and Technical Director, Lucius Pitkin Co.

F. E. CARTER,\* Newark, N. J.—Jewelry alloys, for example 95-platinum 5-iridium, may contain only a couple of tenths per cent of impurities—iridium used being responsible usually for one-tenth. Impurities mean chiefly slight admixtures of the other platinum metals. Actually, the metals used in jewelry today are very pure. When iridium was not so expensive, commercial platinum might contain 1, 2 or 3 per cent iridium, but now it is higher priced than platinum, and the custom is to take out every bit of iridium.

E. M. WISE AND J. T. EASH (written discussion).—With respect to the question of co-present platinum metals, it is only fair to say that the staff of the Acton Refinery of the Mond Nickel Co. has devised and is using refining methods that permit the substantially complete separation of the component platinum metals at moderate cost. To this, rather than to the relative costs of the several platinum metals, may be ascribed the availability of No. 1 platinum of the quality indicated, which is as good as or better than some of the premium grades formerly available.

F. E. CARTER.—It is rather interesting that palladium shows a greater ultimate tensile strength than platinum, both in the hard-worked and in the annealed condition, and still more interesting that the annealed palladium, with a higher tensile strength, also shows considerably higher elongation.

I want to ask why the authors changed to a gas furnace at 1100° and 1200° C., and whether they would expect that to make any difference in the results.

Also, what furnace was used for the results at 1400° C.? I note that all the figures show that 1400° C. was used for platinum and its alloys, except those in Fig. 3—the three on the right. It would seem to me interesting to know the shape of that curve for the platinum-iridium alloys, and I am curious to know why 1400° was used only for the three curves on the left in that figure.

Also, the curves of Fig. 3 show that the elongation at 900° and 1000° C. of the No. 1 platinum is smaller than that of 5 per cent iridium, 20 per cent iridium and 5 per cent nickel alloys. Also, 20 per cent iridium has a greater elongation than 10 per cent iridium after annealing at 900° and 1000°. Five per cent iridium and 10 per cent rhodium appear to have the same elongation at these temperatures.

I should like to have some figures for the elongation and tensile strength at the annealing temperatures used. Take, for example, a platinum-rhodium gauze as used in ammonia oxidation. This runs at, say, 900° C. and it is important to know the strength and elongation at that temperature. It does not matter much what these properties are after the gauze is cooled to atmospheric temperature and taken out. The same applies to the furnace winding wires. If we could know the strength of these wires at temperature, it would be very helpful.

On page 323, the ultimate tensile strength and elongation of the 10 per cent rhodium alloy are remarkable both in the hard and in the fully annealed state.

Temperatures above 1200° C. were used with some of the platinum alloys but not with the palladium alloys. I wonder why, and could they be tried?

I am not in agreement with the drop in the elongation shown in Fig. 9 for commercial palladium at about 900° or 1000° C. We have done some similar work, admittedly on a different size (0.2-in. dia.) and we gave it a more thorough annealing, which probably explains why we found no drop between 800° and 1100° C. in the elongation. Tensile strength also remains fairly constant. Perhaps the authors' 50 per cent reduction was insufficient to get the pure metals into the really hard-worked stage; it is all right for the alloys, but with the pure metals it may not be enough.

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\* Physical Metallurgist, Baker & Co., Inc.

F. G. SMITH,\* Waterbury, Conn. (written discussion).—The sudden drop in elongation between 800° and 1100° C., as indicated in Fig. 9, marked “#1 Cm Pd,” is similar to the drop in elongation of commercially pure copper after annealing at high temperature. It is difficult to explain because the behavior cannot always be predicted. Copper annealed over a range of temperatures usually has a grain size roughly proportionate with the temperature of anneal, up to about 700° C. Annealed above 700° C. it may or may not have a normal grain size. If the grain size remains normal the elongation holds up, but if grain size becomes relatively large the elongation falls off sharply. The latter tendency is most likely to be found with the coppers of highest commercial purity. Even a very small content of silver and/or arsenic tends to inhibit the abnormal grain growth at high temperatures.

The authors state that hardened (that is, alloyed) palladiums do not show this marked drop in elongation. It may require only a very small amount of alloying element to have this effect. This element might be a common constituent of commercially pure palladium and its effect may be overlooked for that reason. Dr. Carter says, “We find no drop between 800° and 1100° C. in the elongation.” The palladium he refers to may be ever so slightly alloyed as compared with the authors’ specimens and still be a high-grade commercially pure palladium. In other words, certain “impurities” may be beneficial; e.g., prevent abnormal grain growth and so improve certain physical characteristics.

G. EDMUNDS,† Palmerton, Pa.—To obtain maximum forming quality in these alloys, is it the usual commercial practice to give them 50 per cent cold reduction, or to take them as they are cold-drawn or rolled and *then* to anneal? If you wish to use some of these alloys for a deep forming operation in commercial work, would you take the wrought alloy and give it an annealing, then a 50 per cent cold reduction, then another annealing, or would you take a cold-worked or hot-worked structure and anneal it without that intermediate cold-rolling reduction?

The reason for my question is that the introduction states that the specific treatment was given the alloys because they are frequently used for deep forming operations, and you wish to develop a high degree of formability in the alloys. I wondered whether the results were directly applicable to commercial practice? We know that annealing results in widely different physical properties, depending upon the initial treatment.

J. T. EASH.—That is true. But is there not a certain amount of cold reduction that can be given a metal beyond which the annealing temperature does not change? We selected this 50 per cent because we knew we could cold-draw all of the alloys to that amount, and we believed that it would yield a representative annealing behavior.

F. E. CARTER.—Of course, an alloy would naturally be worked down as far as possible between annealings. It may be 100 per cent; in some of the softer metals it may be 200 or 300 per cent. As Dr. Eash says, he went to the 50 per cent because he wanted to make comparisons, and with some of these alloys one cannot do too much work between annealings.

G. EDMUNDS.—I think you have brought out the point I had in mind; that some of the alloys might be workable to an extent of 50 per cent cold reduction, which would represent the limit of the workability of those alloys, and that it might be possible to work other alloys to several hundred per cent. Therefore, a comparison based upon an identical treatment of widely different alloys is not a comparison of commercial

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\* Sales Engineer, The American Brass Co.; Metallurgist.

† Research Division, New Jersey Zinc Co.

value. Commercial value comes from comparison of alloys (depending on the alloys themselves) given their ordinary commercial prior treatment.

F. E. CARTER.—Yes, that is true. That is the position I took, that for the pure metals, like platinum and palladium, 50 per cent did not appear to be sufficient working. The other alloys seem to be all right. Some interesting figures were obtained, but I should like to see figures for platinum and palladium, with the materials thoroughly hard worked.

J. T. EASH.—By giving it a greater amount of cold-work, we naturally raised the properties. At the end point, where it was soft, it would be about the same.

G. EDMUNDS.—No, I cannot agree with you on that.

E. M. WISE AND J. T. EASH (written discussion).—No significant drop in elongation of palladium was noted in these experiments except at annealing temperatures in excess of 1000° C. The same applies to unreported experiments on specially purified palladium. Both the No. 1 and specially purified palladium showed an abrupt drop in elongation after annealing at 1100° C., although the selective grain growth was much less marked in the special sample. We have also observed markedly irregular grain growth in other samples of very pure palladium that had been reduced 96 per cent by cold-rolling, so that it seems unlikely that the behavior was due to the particular reduction employed in the present tests.

It is quite possible that very faint traces of impurities including oxygen, rather than the reductions employed, are responsible for these phenomena. Mr. Smith's observations are pertinent and the phenomena noted by him appear to be closely related to those occurring in palladium.

Even small amounts of alloying elements that serve to slightly and uniformly restrain grain growth doubtless would tend to eliminate, or at least reduce, the tendency toward selective grain growth. However, where extreme softness is required the presence of alloying elements is not entirely welcome.

As Carter notes, the elongation of No. 1 palladium is higher than that of No. 1 platinum, although palladium possesses a higher tensile strength, but it should also be noted that the reduction of area of platinum generally is slightly greater than that of palladium.

The safe operating temperature of the large furnace employed for most of the annealing treatments was 1000° C., hence the change in furnaces for 1100° and 1200° C. treatments. The 1400° C. anneals were conducted in a small electric furnace of a special type containing an air atmosphere. As stated in the paper, palladium annealed in the gas furnace and in *vacuo* yielded substantially identical properties. However, it has been observed in practice that in drawing very fine platinum wires intermediate vacuum annealing in sizes below 0.001 in. is very helpful. A good nitrogen atmosphere should be equally suitable.

With regard to the elongations of the iridium-platinum alloys at higher annealing temperatures than those shown in Fig. 3, we may add the following data relating to a 1400° C. anneal. The observed elongations were 26 per cent for 5 per cent iridium; 20 per cent for the 10 per cent iridium and 20 per cent for the 20 per cent iridium-platinum alloys. This annealing temperature is detrimental to the first two alloys and may also result in some loss of iridium if the atmosphere is oxidizing.

The elevated-temperature short-time tensile strengths of well annealed wires of most of these alloys have been determined and may be presented in a later paper. However, in reply to Carter's question, it may be said here that the tensile strengths of C.P. platinum, 5 per cent Ni-Pt and 10 per cent Rh-Pt at 800° C. were 7800, 28,400 and 22,200 lb. per sq. in., respectively, while at 1000° C. they were 4000, 15,700



and 13,600 lb. per sq. in. The elongation of the 10 per cent Rh-Pt was 37 per cent at 800° C. and 51 per cent at 1000° C. These strengths are very high as compared with more familiar alloys and are factors contributing to the successful use of platinum alloys, not only in the situation noted by Carter but also in the filaments employed in long-life telephone amplifiers and in certain important new industrial uses of platinum alloys.

With regard to the comments of Edmunds and Carter on the details of processing, and particularly on the advisability of selecting 50 per cent reduction in area as compared to random and particularly very high reductions, we may state that platinum alloys are generally hot-worked from the ingot, usually by forging, and are finished by cold-rolling or cold-drawing with suitable anneals. With the more ductile materials, not only those here employed but certain base metals as well, high reductions may be employed for commercial reasons despite the resulting tendency in base metals so treated, and probably in the platinum metals as well, to develop undesired preferred orientation. Material finished with 50 per cent reduction effected by cold-drawing is readily available and may be so specified, and would ordinarily be annealed prior to forming operations. Furthermore, it should not be overlooked that intermediate anneals are often required in the course of final fabrication and the intervening reductions are not necessarily very large. It is recognized that the annealing behavior of the more ductile metals, as reflected in hardness and tensile properties, shows marked sensitivity to the previous reduction when this is of the order of 30 per cent or less, but with reductions of the order of those employed in our work (50 per cent) this effect is usually not of much consequence. In previously reported hardness data by Carter reductions of about 66 per cent were employed but 50 per cent was chosen in our investigation in view of the fact that it was at least as suitable and has been quite generally used by ourselves and by many others. The use of assorted reductions, differing with each material, as suggested by one of the discussers, would greatly reduce the utility of the data and would render useful comparisons of properties in any but the annealed state difficult and probably impossible.

We are familiar with the work on the deep-drawing properties of zinc-rich alloys done by Edmunds and his associates in which they found it impossible to correlate the deep-drawing properties of this metal with the usual tensile properties (possibly excepting the reduction of area), and finally adopted a draw die of an arbitrary but reasonable design to develop information applicable to nearly identical operations in the field. It should be pointed out that the hexagonal crystal structure of zinc and its sensitivity to the speed of deformation give rise to special problems not involved with the platinum metals, which normally give little trouble in drawing operations. Likewise, we were not particularly concerned with shell drawing but were desirous of determining the more important and generally recognized properties of variously annealed samples, which would be of broad value to users of platinum metals.

In connection with questions concerning percentage reduction, we are at a loss to understand what the discussers mean by reductions of several hundred per cent, in view of the fact that the reduction in area as generally defined and used by us can approach but not exceed 100 per cent.

Obviously, one series of tests, however conducted, could hardly be expected to indicate the absolute optimum treatment for special operations ranging all the way from coining operations to the beating of leaf, and utilizing material prepared by rolling, swaging, drawing and even beating, but if it serves to furnish satisfactory guidance in the choice of materials and annealing temperatures its object has been accomplished.

## The Role of the Spectrograph and of Minor Elements in Die Castings

BY THOMAS A. WRIGHT,\* MEMBER A I.M.E.

(New York Meeting, October, 1934)

No symposium on die-casting could be complete without consideration of the methods of formula and impurity control. No consideration of control would be complete without discussion of that new tool of the analytical chemist and inspector, the quartz spectrograph. Just as there is an increased appreciation of the possible applications of the die-casting process and of die castings, so too is there, slowly but surely, of the spectrograph.

At present the role of the instrument might well be compared with that of brass or magnesium die castings. Neither is as widely understood or known as they will be. Product specifications are increasing and are getting more explicit and often more rigid. The designer, metallurgist and production engineer or superintendent will be forced to depend more and more on the chemical laboratory. Sampling, as well as analyses, testing and inspection problems will grow. The chemical laboratory must meet its increased responsibility and use of the spectrograph will become more common. Advantages of increased precision, greater speed, lessened labor and often lower costs cannot be ignored.

It will be the purpose of this paper in part to outline the respective fields of chemical and spectrographic analyses and to indicate where one may overlap the other and in part to indicate certain possible sources of contamination of zinc-base die-cast alloys in particular.

### COMPOSITION

*Aluminum.*—Aluminum die castings are expected to conform to the specifications of the American Society for Testing Materials<sup>1†</sup> and the Society of Automotive Engineers<sup>2</sup>. The A.S.T.M. has recognized seven aluminum alloys in Tentative Specification B85-33-T. Two are straight silicon and the remainder are of the copper-silicon type of which alloys VIII and IX have in addition respectively 2 and 4 per cent of nickel, but unlike the others are not covered by S.A.E. as well. All seven call for rigid control of certain impurities. With the exception of alloy XII,

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\* Technical Director, Lucius Pitkin, Inc., New York, N. Y.

† References are at the end of the paper.

which permits a maximum zinc content of 1.50 per cent, tin 0.20 per cent and total other impurities 0.50 per cent, all carry maxima of zinc 0.75 per cent, manganese 0.30 per cent, magnesium 0.10 per cent and tin 0.10 per cent. Iron, however, may be present, inasmuch as 2.50 per cent in four of the copper-silicon type but only to the extent of 2.25 per cent in the others. In the two aluminum-silicon alloys 2.00 per cent is the maximum. Nickel is limited to 0.50 per cent in five of the alloys.

TABLE 1.—*Specifications for Zinc-base Alloys*

Elements	Percentages	
	XXI	XXIII
Aluminum.....	3.5-4.5	3.5-4.3
Copper.....	2.5-3.5	0.10 (Maximum)
Magnesium.....	0.02-0.10 Permissible range.	0.03-0.08
Magnesium.....	0.02-0.05 (0.035) Desired.	0.03-0.06 (0.045)
Tin.....	0.005 Maxima allowed.	0.005
Lead.....	0.007 Maxima allowed.	0.007
Cadmium.....	0.005 Maxima allowed.	0.005
Iron.....	0.10 Maxima allowed.	0.10
Nickel.....	Maxima allowed.	0.015-0.03 (If so specified)

The term "total other impurities," unfortunately not defined, is subject to varying interpretations, but for practical use, in view of the economic value of using secondary aluminum, it may be assumed to mean lead and antimony and possibly chromium. As the permissible total allowed on alloys IV to IX is only 0.20 per cent of "other impurities" chemical analyses for such elements in the finished casting is too expensive and time consuming to be a regular practice.

*Zinc.*—Only two zinc-base alloys are recognized—A.S.T.M. XXI, S.A.E. 921 and A.S.T.M. XXIII, S.A.E. 903. The specifications necessarily are very rigid not only for the added element magnesium but for the impurities tin, lead, cadmium and iron. No maximum for silicon, or rather silica, sometimes found, is set. Specifications slightly modified from A.S.T.M. 86-33T are given in Table 1.

*White Metal.*—No special specifications have been set up by A.S.T.M. for either the tin base or lead-base alloys with or without antimony and/or copper, as the larger proportion of the production as a whole is in the field of bearings that are covered by S.A.E. specifications. In general the composition limits are rather wide and the use of addition metals in minor amounts is not common, although, as stated by Tobias<sup>3</sup>, nickel, sodium, cadmium and magnesium when added will affect the physical properties and zinc, aluminum, bismuth and arsenic are limited

in bearing metals. Spectrographic control is indicated, of course, for the minor, with chemical analyses for the major elements.

*Magnesium.*—The magnesium-base type specifications being new are limited to the one proposed for what is at present known as alloy No. 2. The minimum composition for magnesium is 88 per cent, the range for aluminum is 9 to 11 per cent and the range for manganese is 0.10 to 0.30 per cent, the smaller amount being sufficient, apparently. The maximum impurity limits are copper 0.10 per cent and nickel 0.05 per cent, any larger amounts decreasing the corrosion resistance. According to the last report of Committee B-6<sup>4</sup> other elements often present in appreciable amounts in other magnesium-base alloys appear to have no detrimental effect when present in small quantities in a die casting, and not being classed as impurities, have had no limits set up therefore. Presumably, if present in amounts greater than those within the present scope of spectrographic analyses they might be detrimental.

*Brass.*—There remains, therefore, only one other class of die castings to consider and that too is of recent origin. Few data have been published and comparatively few accumulated. There are no accepted specifications for brass die castings although production to date centers around the 60 per cent copper, 40 per cent zinc, or high-brass type and the high-strength copper-silicon alloy. The high brass will preferably carry approximately 1 per cent tin and from 0.25 to 2 per cent lead, both susceptible of ready chemical control. The addition of aluminum in amounts up to, say, 0.20 per cent may be advisable. Because of the difficulty of determining small amounts of this element chemically, the spectrograph is certainly indicated.

### EFFECT OF IMPURITIES

The effect of impurities in the aluminum die-cast alloys has been the subject of much research not only by various industrial companies for their own information, but through cooperative work. Committees B-3, B-6 and B-7 of the A.S.T.M. have been exceptionally active in this respect. Details are given in the various committee reports. The matter has been summarized with pertinent comment by Rollason and Tour<sup>5</sup> and by Tour<sup>6</sup>.

All the impurities, with perhaps the exception at present of the larger percentages of iron, are within the scope of the spectrograph. In general the effect of these minor elements is considered adverse, although proper balancing may offset this and in certain cases the presence in proper amount may be beneficial or even negligible, depending upon the characteristic or property in question. Thus indications are that iron, manganese, nickel and magnesium, within certain limits, do not appreciably decrease the corrosion resistance of the aluminum-silicon type, but zinc

and tin are detrimental and copper decidedly so. The matter is being studied further.

Zinc and tin produce hot shortness in aluminum die castings and manganese and chromium in small amounts are beneficial, according to Rollason and Tour. Tour tabulates the beneficial and detrimental effects of small amounts of eight elements, although calling attention at the same time to the fact that combinations of two or more may seriously change the effect on the casting properties. Indications are that the mechanical properties are seriously affected as well; for example, by tin, antimony and magnesium. Small amounts of metals are purposely added at times but by and large they usually are present through contamination.

### CONTAMINATION

Impurities, inherent in the raw materials used or present through contamination, can cause immeasurable trouble. No better example exists than the zinc-base die castings. Real reasons exist for the specified maxima of the impurities lead, cadmium and tin, for example. Magnesium within the permissible range is beneficial. Corroborative data to this effect have been assembled and some of the results published. In a corrosion study made some years ago in the laboratories of Lucius Pitkin, Inc. the absolute necessity for keeping those four elements within set bounds was definitely shown. Others have made like studies<sup>7</sup> all leading to the definite conclusion that contamination was more or less disastrous but definitely avoidable with proper control.

Apparently the significance of such data is not yet known or appreciated as it should be, for unnecessarily faulty material is being produced. Contamination, and to a somewhat less extent improper formulation, is responsible for the majority of the actual or embryo failures. An illustration is the case of 142 faulty castings accumulated by the New Jersey Zinc Co. over a period of three years and referred to recently by W. M. Peirce in an unpublished talk before the Detroit Chapter of the American Society of Metals. Again their painstaking studies revealed valuable data; 25 per cent of the causes for failure, and the castings averaged over two causes apiece, were due to improper formula, but almost 40 per cent were plain dirty metal. The polite word is "contamination." Wrong choice of alloy, faulty application, mechanical and finish defects composed the balance.

Aside from dimensional instability, contamination, however, may have other less immediate and less obvious bad effects, depending not only on the amount present of a single impurity but on the sum of the whole or of a group. Loss of impact and tensile strength, and increased difficulty in machining<sup>8</sup>, through either increased abrasive qualities or hardness, may result. When a zinc casting is to be electroplated surface

defects in the plate may occur. According to Castell<sup>9</sup>, porous castings and occluded gases are sources of such plating failures. Where contamination has any appreciable effect upon surface appearance, porosity or shrinkage must be for others to decide.

### SOURCES OF CONTAMINATION

Virgin metals are produced to such high purity standards today that usually there is little reason to fear contamination from that source, notwithstanding that such a metal when used as a base may often compose 90 per cent or more of the final alloy. Certainly this is true of aluminum, zinc, copper, lead and tin. There are different grades, of course, but the limit of impurities is set and in general one may expect to find the analyses substantially as stated. It only remains to choose a grade suitable to the alloy and to the other elements added, except in the case of the zinc alloys, where only one, and that the 99.99 per cent grade, is allowable.

True economy, and making castings to a price, both tend to a maximum use of scrap and secondary metal, neither of which is necessarily less pure than virgin. In fact, it is quite possible that for some metals previous meltings may have even resulted in a reduction of percentage of certain of the elements present in the original virgin metal. Scrap aluminum may have been more or less contaminated from its original use, yet when skilfully sorted, cleaned, reprocessed and remixed, a suitable and even exceptionally desirable product is available. The reliable ingot maker today uses close analytical and in some cases spectrographic control, thus insuring a reliable source often at marked savings. Thus a typical intermediate or "hardener" alloy sometimes used in the zinc die-cast alloys has the formula 55 aluminum, 30 copper, 15 zinc. To be used in the XXI alloy, the maximum safety content allowable would be 0.05 per cent lead and 0.04 per cent tin. Caution indicates that an even greater safety margin be furnished and the reliable ingot maker is prepared to do this.

Aluminum and copper may be, and often are, added directly to the melt in the form of wire or clips and must be considered as a promising source of contamination, the erratic character of which may be limited by pigging with remelt rejects, gates, sprues, etc., etc. Sampling becomes easier. Lack of analytical control becomes less defensible with pigged metal, and when scrap metals are used guesses and assumptions are in the long run far more expensive than control.

After all, most scrap aluminum is really an alloy containing from five to ten elements. Lead, tin, zinc and iron are common contaminants, magnesium will become more common, and as received from the accumulator the scrap may consist of material from a number of varied sources.

Sorting is an art not as readily acquired as some may think and not always practiced as carefully as it might be. Witness the high silica found on occasion in zinc-base die castings or the excessive lead and zinc found in aluminum castings. Loose, heterogeneous material being difficult to sample and analyze, guess can easily be the rule.

It is quite possible that contamination from lead—and to a lesser extent from tin—may well come from the use of what is called “clean” copper wire. An experience of many years sampling, grading and analyzing thousands of shipments of the grades of copper known as No. 1, No. 2 and Light Copper destroys many illusions. In the copper refineries, committed to turning out high-conductivity metal, no chances whatever are taken. Contrary to general belief, the material may be “free of solder” as called for by specifications of the National Association of Waste Material Dealers, and yet not be free of lead, whether washed or not. Rigid compliance is hopeless. Much wire is soldered or spliced, or it will have come from burned lead-covered cable. Ash from burnt wire may carry as much as 25 per cent lead. It is rarely free of at least small amounts. It is not unusual, on analyzing a melted bar of so-called “clean” scrap wire, to find that the lead runs 0.03 to 0.05 per cent, and it must be remembered that there is little call to analyze such a sample for lead except when such wire has been sold as a special high-grade No. 1. In fact, such extra or premium grade is accepted as such fundamentally because the previous origin and use is known and subject to very careful inspection. Briquetted wire must be assumed to carry dangerous amounts of lead and/or tin if in connection with zinc alloy. A “clean” lot of No. 2 might show as much as 0.90 per cent lead and, of course, tin too. Washing burnt wire helps reduce the lead. Copper wire may contain copper-clad with an iron core. The author knows of two cases where clean, new so-called “copper” sheet assaying 1 per cent copper passed through several expert hands without detection of the iron base!

Contamination may be expected to occur also in any plant that makes an extended series of die-cast alloys. This point is recognized sufficiently so that usually great care is taken to remove lead-base or tin-base metal casting not only from the building but even from the same plant. Nevertheless enough chances remain of mixing formula with formula. No. XXI zinc alloy calls for 3 per cent copper but XXIII only permits a maximum of 0.10 per cent. A magnesium-base alloy mixed with either an aluminum or zinc die cast is but one of many other examples of possible trouble. Some of the scrap in the form of obsolete zinc die castings contains high percentages of tin, as might be expected considering that such an alloy was for some time in use. It must also be recalled that at one time prime western zinc was employed and that such die-cast scrap would contain dangerous amounts of lead. Con-

tamination may also occur from tobacco or other foils, plated inserts, solders, bearing metals and other incidental plant materials.

### PURITY CONTROL

Excessive competition, fathered in great part perhaps by the consumer, has encouraged the making of castings to fit a price rather than a quality standard. This in turn has led to a greater temptation to the use of cheap scrap of questionable origin. Composition has apparently too often been assumed, rather than ascertained by analysis, in a still further effort to keep costs down. As a result castings have been produced that have hurt the reputation of good as well as indifferent die-casters of the zinc alloys. Such a condition is a real temptation for a large consumer to install his own die-casting equipment. Such a duplication of production capacity would extend the vicious cycle of unrestrained competition.

Purity control, then, is as necessary as formula control, and there are only two methods of obtaining the insurance. One is the choice and selection of raw materials; the other is analysis. Both should be practiced, for the premium is after all small for the amount and value of the product. Contrary to general belief, analytical control is not dead overhead to be cut down at every opportunity and to be reluctantly used if at all. Some of the money so freely spent on advertising and other sales expense could return far better dividends if used in controlling and raising quality standards. There is no sounder basis for advertising than facts.

A study of the advertising policies of the most sound and successful metal companies will show how large the laboratory looms. In some noted cases the laboratory and sales departments work hand in hand with the former, always supplying the facts on which to base the claims, sometimes giving the final push that puts over the sale, exercising a veto power on the advertising and even at times writing the text.

Two forms of analytical control are available today. One, the older and more familiar chemical analysis; the other, the newer and less known spectrographic analysis. Both have their uses. The determination of the major elements is best carried out chemically. Minor metals, which of course include the impurities, are best determined on the spectrograph. In many cases either method may be used, so far as necessary precision is concerned. Actual time required, speed, cost of reagents, etc. and availability will often be controlling factors. So too will be the number of samples and the number and type of determinations. Not all companies can afford to have a laboratory manned by competent chemists and not all laboratories can afford to have a spectrograph. Yet no company is small enough or large enough to forego composition control.



## RELATIVE COSTS

Laymen and even engineers often ask, for example, "How much does a lead determination cost?". One might as well ask the same for a die casting or automobile. The cost depends upon the nature of the metal or alloy in which the lead is present and upon the amount and precision required. The determination of lead in high-grade special zinc would cost much more by chemical analysis than that of lead in prime western, yet when performed by means of the spectrograph the cost would be less.

The full chemical analysis of a zinc-base die casting for the same precision is a long, tedious and rather expensive process. Spectrographic analysis will give in an hour if need be a result that would take many hours by chemical analysis. In certain types of specification control, where certain elements may be reported as "not more than" or "less than" the specification figure, the spectrograph gives a still quicker answer, at less cost and often with greater assurance.

In plant-control work, where a qualitative or semi-quantitative result quickly obtained is of immeasurable value, the spectrograph is again superior. For determination of aluminum and high copper in zinc-base die castings chemical analysis is at present the best, as it is in determining copper, silicon and iron in the aluminum die-cast alloys. So far as precision alone is concerned, the spectrograph is outstanding in determinations such as tin, lead and magnesium in either zinc or aluminum.

## SPECIFICATION CONTROL

The ever-present tendency among engineers to fit particular alloys to particular needs results in more rigid specifications. Growing consumer consciousness is accompanied by an inquisitive spirit and a "show-me" attitude. This awakening is being encouraged by government policy, standardization societies, sales engineering staffs, cooperative buying agencies and lectures, magazine articles and in a thousand and one other ways. Continued impetus is being given by trade-practice provisions of Codes and trade-practice standards of the Department of Commerce.

The producer of die castings, then, may either voluntarily exercise the needed purity control or later on yield to consumer demand for certification of quality. If such assurance is not given, only three alternatives remain; the consumer will turn to some other producers or some other product; he will demand the privilege of inspection, as does the Navy, for instance; or he will make his own castings.

Economically, it should be obvious that in the long run defective or reject castings cost the producer even more than unnecessarily pure ones. Consumers are awakening to the cold, hard facts that defective castings result in consequential losses far exceeding the assumed savings on

low-price products. Such a realization builds up a sales resistance of no mean proportions. The resentment may reflect on the producer in question. It may harm an entire industry.

### CONCLUSION

The conclusion seems evident. For the producers, formula must be controlled by chemical and/or spectrographic analyses of the raw materials used and of the current production. Contamination is best avoided and all minor but important elements controlled within the permissible limits by spectrographic analyses, or tests where the latter will suffice.

For the consumer, unless certification is practiced by the producer, insurance of acceptable castings can only be had by judicious sampling and spectrographic inspection in order that questionable material may be rejected promptly and returned. Under such a policy the interests of the responsible producer and large and small consumer will be protected. Die castings will not only hold their own but will find extended uses in fields where needlessly disappointing castings may have created an impression that they were not all they were claimed to be.

The premiums spent for fire or workmen's compensation do not, valuable as the practice is, prevent damage. Small as is the pro rata premium for analytical control, whether performed in one's own or an experienced outside laboratory, that premium will insure the proper formula in the casting as delivered. It will insure control of contamination if the spectrograph is utilized.

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# Phase Changes during Aging of Zinc-alloy Die Castings, I—Eutectoidal Decomposition of Beta Aluminum-zinc Phase and Its Relation to Dimensional Changes in Die Castings

BY M. L. FULLER\* AND R. L. WILCOX,\* MEMBERS A.I.M.E.

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OWING to the nature of the die-casting process, freshly cast alloys are undoubtedly not at equilibrium from the standpoint of alloy phase relationships. After casting, therefore, they tend to undergo phase changes, with the ultimate effect of reaching a state of equilibrium at the aging temperature, beyond which no further change takes place. This phase alteration undoubtedly is one of the primary causes of the changes in dimensions and physical properties that zinc-alloy die castings undergo during aging. It is planned to report on this problem in a series of papers of which this is the first.

The writers have made a study of commercial zinc die-casting alloys over a period of several years, utilizing the X-ray diffraction technic of determining the phase composition changes in the alloys. Up to the present, two principal phase changes have been observed which are capable of causing dimensional changes: (1) the segregation of secondary constituents from the zinc-base solid solution and (2) the beta aluminum-zinc decomposition. The latter is the subject of the present paper and studies on the former will be reported upon at a future time.

## SCOPE OF STUDY

In the present investigation a special technic for the study of the beta phase in zinc-alloy die castings has been developed, making possible the determination of the period of existence of the beta phase after casting.

The pure beta constituent and its decomposition have been studied in detail. The effect of magnesium and copper on the velocity of the decomposition is reported. The heat of decomposition, the eutectoid temperature and the accompanying density change have been measured. The density change has been calculated from data on crystal structure and the result thus obtained has been compared with the actual change.

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\* Investigators, Research Division, The New Jersey Zinc Co., Palmerton, Pa.

The possible influence of the beta decomposition on the shrinkage in freshly cast zinc-alloy die castings is estimated.

### REVIEW OF PUBLISHED WORK

Partly because of their commercial importance and partly because of their great scientific interest, the zinc-aluminum alloys, particularly the beta phase, have been the subject of many papers. The most authoritative work has been that of D. Hanson and M. L. V. Gayler,<sup>(1)\*</sup> whose equilibrium diagram is generally accepted as being essentially correct. The solid boundary of the alpha phase (solid solution of aluminum in zinc) has been determined by W. M. Peirce<sup>(2)</sup> and the corresponding boundary of the gamma phase from 25° to 250° C. has been given by W. L. Fink and K. R. Van Horn.<sup>(3)</sup> Subsequent to the work of Hanson and Gayler, equilibrium diagrams were published by T. Tanabe<sup>(4)</sup> and T. Ishihara.<sup>(5)</sup>

The first workers to report on the beta eutectoid were W. Rosenhain and S. L. Archbutt,<sup>(6)</sup> whose determination of the eutectoid temperature of 256° C. has been most generally quoted. Tanabe and Ishihara have also determined this temperature, offering 270° and 280° C., respectively. Hanson and Gayler were the first to observe the peculiar nature of the beta constituent. They concluded that beta was not an intermetallic compound, as had hitherto been supposed, but a solid solution of which the structure was essentially different from that of the neighboring solid solutions.

Appreciating the suitability of the X-ray diffraction technic to the study of the structure of the beta constituent, The New Jersey Zinc Co. in 1928 undertook such an X-ray study at the Palmerton Laboratory and G. Edmunds, of this laboratory, who was then engaged in research work at Yale University, undertook a similar study.<sup>(7)</sup> Some of the results of these researches are being published with this paper for the first time. The principal finding was that beta is crystallographically identical with gamma and therefore was not similar to the usual type of intermetallic compound. The two phases differ only in lattice parameter by virtue of the difference in composition. This work was done upon pure aluminum-zinc alloys, the X-ray observations being made on the alloys while they were maintained above the eutectoid temperature.

Subsequently, M. v. Schwarz and O. Summa,<sup>(8)</sup> working upon quenched alloys in which the beta decomposition was inhibited by 0.1 per cent magnesium in the alloy, corroborated the finding that beta was crystallographically identical with gamma. They offer a hypothesis for the mechanism of the decomposition, which will be discussed later in this paper.

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\* Numerals in parentheses refer to the bibliography at the end of the paper.

Independently, Schmid and Wasserman had been working on this problem. The results of their work were reported at a colloquium of the Kaiser Wilhelm Institut für Metallforschung in June, 1932, but aside from an abstract<sup>(9)</sup> and a brief note,<sup>(10)</sup> an account of their work apparently has not been published. They agree with the conclusions of Schwarz and Summa with respect to the crystalline structure of beta, and further state that in passing from pure aluminum through the range of gamma and beta the aluminum lattice is contracted at a uniform rate of about  $0.00085\text{\AA}$ . per atomic per cent zinc. The uniformity of this contraction with increasing zinc content of the face-centered cubic lattice is not in agreement with the data obtained in this laboratory or with that published recently by E. A. Owen and J. Iball.<sup>(11)</sup>

Owen and Iball have made a survey of the aluminum-zinc alloys using X-ray methods. They emphasize in their paper that their work must be considered preliminary and incomplete. They agree with the results obtained by previous workers on the structure of beta but their conclusions on the positions of the various phase boundaries would indicate that the presently accepted diagram must be greatly modified. The present authors are not in a position to criticize the work of Owen and Iball in this regard, except to point out that the beta eutectoid temperature proposed by the latter ( $300^{\circ}$  to  $310^{\circ}\text{C.}$ ) is undoubtedly much too high, a point that will be discussed more fully later. Owen and Iball are to be commended for demonstrating by X-ray patterns for the first time the dual phase structure in the beta plus gamma region. This is particularly difficult on account of the small difference between the lattice dimensions of the two phases in this region.

Recent studies on the velocity and mechanism of the transformation have been reported by H. Meyer<sup>(12)</sup> and also by W. Bugakow<sup>(13)</sup> using observations on hardness, electrical conductivity and density.

E. A. Anderson, of this laboratory, working at Yale University<sup>(14)</sup> in 1923, investigated the effect of various metallic impurities on the velocity of the beta decomposition and on the accompanying density change. Notably, copper and magnesium were found to greatly inhibit the decomposition. Some of the results of this work will be discussed later.

Independently W. Fraenkel and E. Scheuer<sup>(15)</sup> observed the inhibiting effects of copper and magnesium. Later Fraenkel and Wachsmuth<sup>(16)</sup> made dilatometric studies of the decomposition.

Very recently R. G. Kennedy, Jr.<sup>(17)</sup> has published the results of a study of the beta constituent and its decomposition, purporting to correlate the density change accompanying the beta decomposition with the shrinkage in freshly cast zinc-alloy die castings. While interesting studies on the decomposition of the pure beta phase were reported, the conclusions drawn with respect to the significance of the beta decomposition to dimensional changes in die castings are in error. This is due to the fact

that the true effect of magnesium was not observed. Kennedy offers X-ray evidence to show that magnesium does not prevent the beta decomposition and then shows dilatometric data in which the magnesium-bearing beta (0.21 per cent Mg) shows nearly no shrinkage with aging up to 6 days. The failure of the alloys to shrink in spite of the fact that the beta apparently has decomposed (by X-ray examination) is explained by the statement that, "Evidently the shrinkage which accompanies the change  $\beta \rightarrow \alpha + \gamma$  has been compensated for, presumably by an expansion caused by precipitation of some magnesium compound."

Aside from the consideration that 0.21 per cent magnesium would be unlikely to produce enough precipitated compound to cause an expansion of 0.3 per cent, the results of Kennedy on the X-ray study are undoubtedly in error. Schwarz and Summa,<sup>(8)</sup> and Schmid and Wasserman,<sup>(9,10)</sup> of whose work Kennedy apparently was unaware, definitely showed that the beta constituent could be retained for a considerable time at room temperature by the presence of magnesium in the alloy. Later in this paper it will be shown that the complete decomposition of beta containing magnesium is not affected until an aging of 7 weeks has elapsed, according to X-ray examination and to shrinkage measurements.

## DECOMPOSITION OF BETA ALUMINUM-ZINC IN ZINC-ALLOY DIE CASTINGS

### *Rate of Decomposition of Beta with and without an Inhibitor*

As previously noted, the first study of the rate of decomposition of the beta constituent from this laboratory was performed by E. A. Anderson.<sup>(14)</sup> In this work, it was found, by measurements of the temperature rise in alloys quenched from the beta region, that when the reaction took place at 0° C. the decomposition became complete in 3¼ min., rising to a maximum temperature of 84° C. (alloy wrapped in insulating material to prevent loss of heat). With the reaction taking place at 20° and 50° C., the times for complete decomposition and the maximum temperature attained were 1¾ min. to 108° C. and 1⅛ min. to 133° C., respectively. In determining the effects of impurities on the rate of decomposition, various metals in the amount of 1 per cent were added to the beta alloy and the series of thermal analyses previously carried out for the pure beta alloy were repeated. In this way it was found that copper and magnesium, among other elements, prevented the decomposition from taking place, within the duration of the tests (5 min.), when the quenching temperature was less than 46° C. for the copper-bearing alloy and less than 65° C. for the magnesium-bearing alloy.

The present authors in making X-ray studies of freshly cast zinc-alloy die castings have found that the beta phase was indeed present

in certain of the alloys but that it decomposed within the first week of aging. The details of this work will be described in a later section of the paper.

On account of the marked inhibiting effects of copper and magnesium (one or the other or both of which are present in modern zinc die-casting alloys) it has been generally considered that the beta phase decomposed more slowly in die castings than these X-ray studies showed. It was decided, therefore, to study the beta decomposition further, and alloys of the compositions given in Table 1 were prepared. High-purity zinc (99.99+ per cent Zn) and a reasonably pure grade of aluminum (99.7 per cent Al) were used.

TABLE 1.—*Composition of Alloys*

Alloy No.	Zn	Al	Cu	Mg
4456	80 0	20.0		
4458	79.9	20.0		0.1
4801	77 6	22.3		0.1
4784	77.6	21.4	1.0	
4783	75 6	21.4	3.0	

#### *Thermal Analysis of Alloys without Inhibitor and with Copper as Inhibitor*

For the determination of the temperature rise accompanying the decomposition, the alloys were cast in rod form, 4 in. long and  $\frac{7}{8}$  in. in diameter. These rods were machined into 2 by  $\frac{5}{8}$ -in. rods and a 0.040-in. hole was drilled in the end of each specimen as a recess for the thermocouple. The alloys without an inhibitor and with copper as inhibitor were thus prepared.

The specimens were annealed for 18 to 24 hr. at 350° to 375° C. and quenched in water at 20° C. The quenched specimens were placed in a special Sil-O-Cel container within a few seconds of quenching, a thermocouple was inserted in the 0.04-in. hole, and the spontaneous rise in temperature was measured at regular intervals, by means of a potentiometer. The data obtained in this manner were plotted in the form of time-temperature curves, which are taken as a measure of the rate of decomposition of the beta phase. The time required to reach a maximum temperature is generally assumed to be coincident with the time to effect complete decomposition.

The data obtained in this manner are plotted on the curves of Fig. 1. The pure beta alloy, No. 4456, containing no inhibitor decomposed in  $1\frac{1}{2}$  min., attaining a maximum temperature of 99.3° C. from an initial temperature of 20° C. The alloy containing 1 per cent copper, No. 4784, became completely decomposed in 58 min., attaining a maximum tem-

perature of 78° C. The alloy containing 3 per cent copper, No. 4783, required a longer time to decompose; 72 min. with a maximum temperature of 80° C. The great retarding effect of copper is clearly shown by these experiments.

That the beta had truly decomposed was checked by X-ray examination of the alloys, which clearly disclosed that the alloys were no longer single-phase beta but a mixture of alpha and gamma.

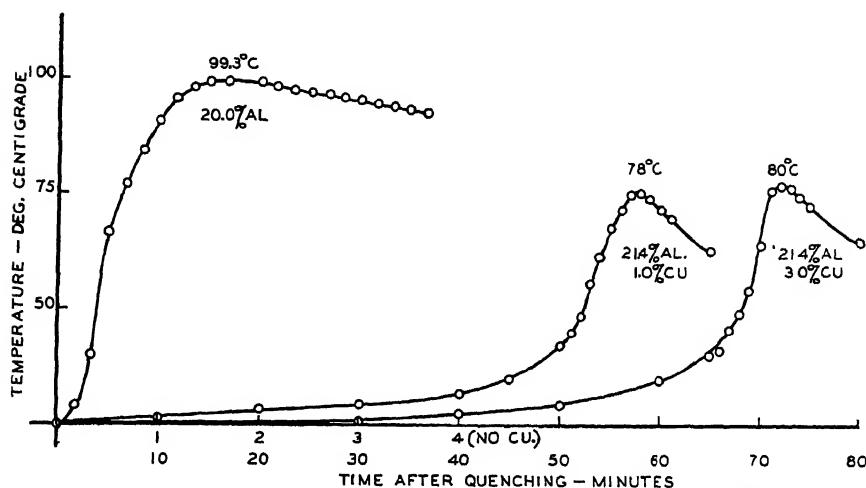


FIG. 1.—RATE OF DECOMPOSITION OF BETA WITH AND WITHOUT COPPER, AS INDICATED BY ACCOMPANYING RISE IN TEMPERATURE.

### *X-ray Analysis of Alloys with Magnesium as Inhibitor*

The alloys containing magnesium as inhibitor, Nos. 4458 and 4801, decomposed so slowly that thermal analysis was impractical. X-ray examination and dimensional change measurements provided suitable means of study.

The alloys for X-ray analysis were cast as small bars  $\frac{1}{2}$  by 1 in. in cross section. These were annealed 40 hr. at 300° C. and quenched. The quenched specimens were hot-rolled (about 200° C.) to 0.060 in. and this material was cut into specimens of convenient size for X-ray analysis. The specimens were then annealed 24 hr. at 325° C. and quenched.

One set of specimens was allowed to age at room temperature and another at 100° C. The specimens were periodically subjected to X-ray examination. The specimens aged at 100° C. were held for definite periods in an oven at that temperature and quenched prior to X-ray examination. The X-ray study was carried out by the back-reflection technic, an exposure of about 3 hr. being required.



By means of the X-ray examination, it was found that as aging progressed the beta content of the alloy gradually diminished with the simultaneous formation of alpha and gamma. The first evidence of alpha was obtained after three days of room-temperature aging or 2 min. of 100° C. aging. The gamma pattern appears somewhat later, its tardiness being due probably to the lower X-ray reflecting power of gamma in comparison to alpha rather than to any actual difference in time of formation of the two phases. The X-ray diffraction lines of gamma are readily distinguished from those of beta, since a difference of 1.4 per cent in lattice dimensions exists between the two phases when the eutectoid is formed at room temperature or at 100° C.

Thus the progress of the decomposition was followed until after aging for 32 days at room temperature or 75 min. at 100° C. the beta phase could barely be detected. The succeeding measurements after aging for 43 days at room temperature and 105 min. at 100° C. revealed that the decomposition had been completed between 32 and 43 days at room temperature and 75 and 105 min. at 100° C.

This work was carried out on two alloys, 4458 and 4801, the one containing a little less and the other a little more aluminum than the eutectoid composition of 21.6 per cent aluminum ( $\text{Al}_2\text{Zn}_3$ ). Identical results were obtained with the two alloys.

#### *Measurements of Dimensional Change on Alloys with Magnesium as Inhibitor*

The large increase in density that accompanies the beta decomposition makes it possible to follow the course of the decomposition by measurements of dimensional change. This has been done by many of the previous investigators, using the dilatometer or simple density measurements. For the purposes of the present investigation, it was decided to use the technic customary for the study of dimensional changes in die-cast test specimens; viz., micrometer caliper measurement of the lengths of test bars.

One of the alloys containing magnesium, 4458, was used in this test. The alloy was cast in rods  $\frac{7}{8}$ -in. dia. and 4 in. long. These rods were machined into cylindrical test specimens,  $\frac{5}{8}$ -in. dia. and  $2\frac{1}{2}$  in. long with plane-parallel ends. The specimens were subjected to the preliminary annealing and quenching, aging at room temperature, and aging at 100° C., to which the X-ray specimens were subjected. The lengths of the bars were measured periodically, yielding the data shown on Fig. 2. The 100° C. specimens were removed from the furnace after definite periods of aging, quenched and measured at room temperature.

If it is assumed that the time for maximum shrinkage is coincident with the time for complete decomposition (disregarding possible shrinkage effects due to changes in alpha or gamma) the beta completely decom-

posed after about 7 weeks at room temperature or 100 min. at 100° C. These reaction times are in agreement with the X-ray results.

The shrinkage resulting from the decomposition of beta is the same after room-temperature aging as after 100° C. aging, within the limits of error. This amounts to a shrinkage of 0.29 per cent.

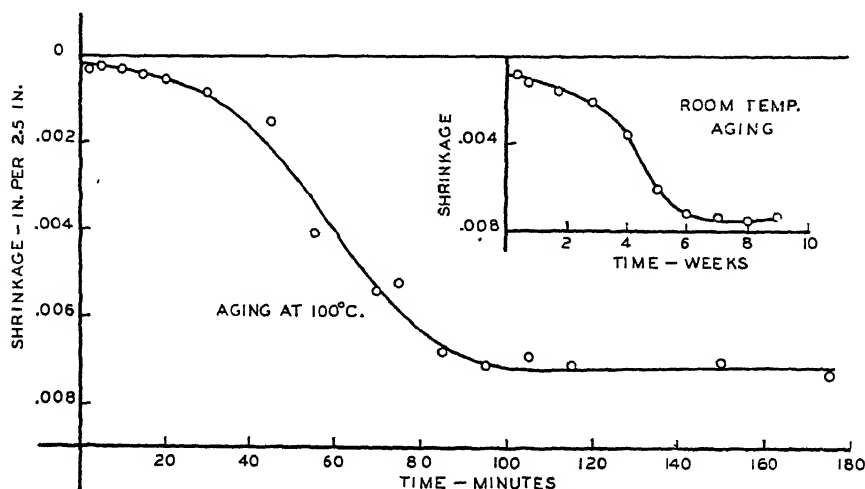


FIG. 2.—RATE OF DECOMPOSITION OF BETA WITH MAGNESIUM, AS INDICATED BY ACCOMPANYING SHRINKAGE.

#### *Calculation of Dimensional Change during Decomposition of Beta*

From crystal-structure data, it is possible to calculate the densities of the beta phase and the products of its decomposition, alpha and gamma. Making the assumption that beta decomposing at 25° C. yields alpha and gamma corresponding to equilibrium at 25° C., the calculation given in Table 2 may be made. On the basis of the atomic

TABLE 2.—*Calculation of Densities*

Beta (21.6 per cent Al) → Alpha (0.25 per cent Al) + Gamma (2.7 per cent Zn)

	Lattice Parameters, Å.		Average Atomic Volume, Å. <sup>3</sup>	Aluminum	
	<i>a</i> <sub>0</sub>	<i>c</i> <sub>0</sub>		Weight, Per Cent	Atomic, Per Cent
Beta.....	3.991		15.89	21.6	40.0
Alpha.....	2.660	4.938	15.13	0.25	0.60
Gamma.....	4.039		16.47	97.3	98.87

percentages given in this table, the percentage of the total number of atoms in the alpha plus gamma mixture which are crystallized on the gamma lattice is 40.09 per cent. Therefore, in the alpha plus gamma eutectoid 40.09 per cent of the atoms have an average atomic volume of

16.47 $\text{\AA}$ .<sup>3</sup> and 59.91 per cent have an average atomic volume of 15.13 $\text{\AA}$ .<sup>3</sup>, or an average of 15.67 $\text{\AA}$ .<sup>3</sup> for the composite eutectoid.

Thus the change in atomic volume from beta to the products of its decomposition is from 15.89 to 15.67 $\text{\AA}$ .<sup>3</sup>, a decrease in volume of 1.38 per cent or a shrinkage in length of 0.48 per cent. The calculated shrinkage of 0.48 per cent is higher than the experimentally observed shrinkage of 0.29 per cent. This difference may be due to one or both of the following causes: (1) The assumptions on the compositions of the lpha and gamma phases in the eutectoid may be inexact and therefore may cause an error in the calculated shrinkage. For example, if the zinc content of the gamma phase was actually higher than the assumed value of 2.7 per cent, the calculated shrinkage would be less 2. (2) The strains set up in the polycrystalline alloy by the net shrinkage\* of the individual crystals may not have been sufficient to cause the metal to completely take up the voids created by the shrinkage.

#### *Decomposition of Beta in Zinc-alloy Die Castings*

The beta and gamma aluminum-zinc phases are not present in sufficient concentration in zinc-alloy die castings to be detected by the usual technic of X-ray examination. For this reason a special technic was developed whereby the beta and gamma phases are concentrated by removal of the phases richer in zinc. The die-casting alloy is etched deeply with an etching solution of chromic acid and sodium sulfate (20 grams  $\text{CrO}_3$ , 3 grams  $\text{Na}_2\text{SO}_4$ , 100 c.c. water). This solution etches away the zinc-rich phases more rapidly than it does the beta and gamma aluminum-zinc phases. The beta and gamma, after the etching, remain concentrated with respect to the phases richer in zinc, as a loose powder on the surface of the casting, which is removed and dried on filter paper. An X-ray powder pattern of this material is obtained, using the General Electric X-ray diffraction apparatus, requiring an exposure of 16 to 24 hr. The difference in lattice dimensions between the beta and gamma is sufficient to permit clear resolution of their diffraction patterns on this apparatus.

Realizing the possibility that the etching procedure might accelerate the beta transformation or otherwise change the condition of the phases from that existing before etching, the technic was tested by the following experiment. An alloy containing 10.0 per cent aluminum and 0.1 per cent magnesium, balance zinc, was annealed 24 hr. at 325° C. and quenched. This specimen should have been entirely alpha and beta if the magnesium had effectively prevented the decomposition of the

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\* The gamma crystals have a greater atomic volume than the beta crystals from which they were formed, whereas the alpha crystals have a lower atomic volume than the beta. The net result is a eutectoid of smaller average atomic volume than beta, or a net shrinkage in the composite alloy.

beta. On the third day after quenching, the alloy was etched with the  $\text{CrO}_3\text{-Na}_2\text{SO}_4$  etching solution, which apparently etched the specimen evenly. The large quantity of beta present was sufficient to prevent disintegration, as occurred in the etching of the die casting. X-ray examination revealed that the alloy consisted of alpha and beta alone. This experiment demonstrated that the etching procedure does not destroy beta or cause it to transform to alpha and gamma. Accordingly, the foregoing method was applied to the examination of freshly cast zinc-alloy die castings. Three of the commercial zinc-aluminum die-casting alloys were tested. The compositions are listed in Table 3.

TABLE 3.—*Composition of Zinc Die-casting Alloys Tested*

Trade Name	Nominal Composition			
	Aluminum	Copper	Magnesium	Zinc <sup>a</sup>
Zamak-2.. . . . .	4.1	2.9	0.04	Balance
Zamak-3..... . .	4.1	None	0.04	Balance
Zamak-5 .....	4.1	1.0	0.04	Balance

<sup>a</sup> Zinc 99.99+ per cent pure.

It was found that beta was present in freshly cast Zamak-2 and Zamak-5 but if present in Zamak-3 beta was completely decomposed in less than one day of room-temperature aging. The beta in Zamak-2 and Zamak-5 decomposes rapidly. A test on Zamak-5 after one day of aging showed that the beta was present in only a small amount, gamma being far more predominant. Tests made on Zamak-2 and Zamak-5 after 6 and 9 days aging, respectively, showed no beta. Reexamination of die castings of the three alloys after 4 to 5 weeks of aging gave no evidence of beta. It cannot be stated whether or not the alloy contains its full complement of beta immediately after casting. Under the conditions of X-ray examination, considerable aging takes place before the X-ray exposure has been completed and in every case the gamma phase was found in addition to the beta phase.

In single-phase beta alloys quenched from a temperature of beta stability, magnesium retards the beta decomposition, so that 7 weeks aging is required to effect complete decomposition, whereas in Zamaks 2, 3 and 5, each containing magnesium, the decomposition is effected within one week. This difference in time of decomposition may be due to one or more of several factors, as follows:

1. The die castings were not so rapidly cooled from above the eutectoid temperature as the experimental single-phase beta alloys were cooled, since in the former case the usual die-casting practice of air-cooling was followed and in the latter case the alloys were quenched in water.

2. The large amount of alpha, together with the beta initially present in die-casting alloys, may accelerate the decomposition. This effect has been demonstrated experimentally by R. G. Kennedy, Jr.<sup>(17)</sup>

3. The amount of magnesium available for the purpose of retarding the beta decomposition was probably different for the two cases.

It is interesting to note that the stability of beta is greater in zinc-aluminum die-casting alloys containing copper in addition to magnesium, owing probably to the additional inhibiting effect of copper. This effect was demonstrated experimentally for the single-phase beta alloy.

### *Effect of Beta Decomposition on Dimensional Changes in Zinc Die Castings*

Experimentally it has been demonstrated that:

1. Magnesium and copper greatly retard the beta aluminum-zinc decomposition into alpha and gamma.

2. The beta constituent decomposes much more rapidly in zinc-alloy die castings than in single-phase beta alloys quenched from a temperature of beta stability. Thus, in Zamak-3, containing magnesium but no copper, the beta, if present, decomposes in less than one day. In Zamak-2 and Zamak-5, containing copper and magnesium, the beta is definitely present in fresh castings but decomposes in less than one week.

3. The shrinkage resulting from the decomposition of a single-phase beta alloy is 0.29 per cent. Expressed in the terminology of the die-casting technologist, the shrinkage is 0.017 in. in 6 in. (the customary length of test bars).

In order to estimate the possible shrinkage effect of the beta decomposition in die castings, it is necessary to estimate the beta content of the freshly cast alloy. If it is assumed arbitrarily that the aluminum content of the zinc-base solid solution is 1 wt. per cent (2.38 atomic per cent) and of the beta phase 18 wt. per cent (34 to 36 atomic per cent) in the freshly cast Zamak, the beta phase amounts to 20.9 per cent by volume of the composite alloy in Zamak-3 (less in the cases of the copper-bearing Zamaks 2 and 5). Thus, if the freshly cast Zamak contains its full complement of beta, the decomposition of beta could account for a shrinkage of 0.058 per cent (20 per cent of 0.29) or 0.0034 in. in 6 inches.

In considering calculations of this type, it should be borne in mind that the actual ratio of undecomposed beta in the die casting to the calculated maximum beta content is not known. Certainly, under die-casting conditions some beta may decompose before the die can be opened, the casting removed and allowed to cool. The calculations set forth the maximum possible dimensional change due to the decomposition of beta. The actual change from this source is probably less.

From measurements of the actual shrinkage in die castings, it has been found that the shrinkage proceeds rapidly but with a diminishing

rate during the first few weeks of aging, becoming practically immeasurable after five weeks. The shrinkage after five weeks of room-temperature aging of Zamaks 2, 3 and 5 amounts to 0.0067, 0.0039 and 0.0050 in. in 6 in., respectively.

On account of the continued shrinkage of the castings after the beta has completely decomposed, it seems highly probable that the beta decomposition is not the sole cause of shrinkage. Abundant evidence has been obtained to indicate that other phase changes are causing shrinkage. This is shown by the fact that annealing at temperatures above 100° C. and below the eutectoid temperature causes an expansion. If the castings are allowed to age at room temperature following such an annealing they again undergo shrinkage. All of these changes take place after the original beta has decomposed and at temperatures below the eutectoid temperature. The high rate of shrinkage during the first week of aging is probably largely due to the beta decomposition, but the subsequent shrinkage is probably due to other phase changes, which the writers plan to report on at a later time.

#### ADDITIONAL NOTES ON THE BETA DECOMPOSITION

##### *Heat of Decomposition*

The heat evolved during the beta decomposition was measured with a calorimeter, specially constructed for this type of work. A vertical tube furnace was used for preheating the specimen to a temperature above the eutectoid temperature. The calorimeter was placed under this furnace in such a manner that the specimen, when released, would drop instantly through the spring trapdoors of the several insulating jackets into the water of the calorimeter.

Two zinc-aluminum alloys, each containing 20 per cent aluminum, one with 0.25 per cent magnesium and one without magnesium, were used for determining the heat of decomposition. A determination of the heat evolved was made when each alloy was dropped from a temperature of 280° C. into the water of the calorimeter at 19.5° C. The alloy without magnesium decomposed into alpha and gamma; the alloy with magnesium did not decompose. The difference in the heat evolved by the two alloys is the heat of the eutectoidal decomposition of beta.

By this procedure, the heat of decomposition of beta was found to be 7.39 calories per gram of the 20.0 per cent aluminum alloy. The calculations assume that the presence of the magnesium does not alter the specific heat of the alloy. The precision of this determination is about 3 per cent. The heat of decomposition per mol of  $\text{Al}_2\text{Zn}_3$  can be calculated as  $1850 \pm 50$  calories, neglecting the fact that the alloy is not exactly of the composition  $\text{Al}_2\text{Zn}_3$  (21.6 per cent Al).

*Temperature of Decomposition*

Thermal analysis by the determination of heating and cooling curves was made on an alloy containing 15.2 per cent aluminum, balance zinc. The thermal analysis was performed by a refined procedure for which the writers are indebted to Mr. C. F. Homewood, of this laboratory, who developed the apparatus and method and to Mr. J. R. Bossard, who made the measurements.

The alloy was melted in a Pyrex-lined graphite crucible and allowed to solidify with a Pyrex thermocouple protecting tube immersed in the melt. For the heating-curve work the alloy was allowed to cool overnight to about 100° C. and the temperature increased to 150° C. in the morning before readings were taken.

The temperature of the furnace was varied gradually and uniformly by means of a motor-driven graded rheostat. Periodic temperature readings were taken from carefully calibrated iron-constantan couples with a White potentiometer. The temperature of the alloy and the differential between the alloy and furnace temperatures were taken. The differential temperature curve provided a sensitive check on the position of the thermal arrests indicated by the temperature changes of the melt.

Using three different rates of heating and cooling, the data in Table 4 were obtained:

TABLE 4.—*Thermal Arrests at Beta Aluminum-zinc Eutectoid*

Heating Curve		Cooling Curve	
Rate, Deg. C. per Minute	Arrest, Deg. C.	Rate, Deg. C. per Minute	Arrest, Deg. C.
1 3	276.8	1 7	258 9
1.0	278 8	0 90	260.2
0 67	277.6	0.57	261 7

In each of the cooling curves the temperature of the alloy increased nearly 1° C. after the initial arrest, probably because of the heat evolved during the decomposition. The heating curves showed sharp arrests, with one of the curves showing a drop in temperature of 1.2° C. after the initial arrest, probably due to the absorption of heat in the formation of beta. Table 4 gives the initial arrests for all cases.

The cooling-curve data show that as the rate of cooling is made slower the thermal arrest is higher. The heating-curve data show no trend with respect to the rate of heating. These data suggest that the alloys supercool in approaching the eutectoid temperature from a higher temperature and do not superheat in approaching the eutectoid tempera-

ture from a lower temperature. Rosenhain and Archbutt<sup>6</sup> determined the eutectoid temperature as 256° C., a temperature that appears to be too low in the light of the data of this paper as well as that of Tanabe<sup>4</sup> (270° C.) and Isihara<sup>5</sup> (280° C.). Rosenhain and Archbutt's value of 256° C. was determined by the cooling-curve method, using much more rapid rates of cooling than those used in this paper. The authors do not feel that the data presented in the foregoing are sufficient to fix precisely the eutectoid temperature but believe that the temperature indicated by the heating-curve data is more nearly correct than that from the cooling-curve data.

### *Structure of Beta and Mechanism of Its Decomposition*

Crystallographically, beta is identical with gamma. Both show the face-centered cubic structure with identical relative line intensities in their X-ray powder diffraction patterns, differing only in lattice dimensions. X-ray diffraction patterns of 20 aluminum-zinc alloys ranging in composition from pure zinc to an alloy of 84 per cent aluminum content, have been made in this laboratory while the alloys were maintained at 285°, 365° and 425° C. In no case was any structure but that of the face-centered cubic for the beta and gamma constituents, and of the hexagonal close-packed for the alpha constituent, noted.

The lattice measurements of the face-centered cubic alloys did not show the regular and uniform variation with composition that was found by Schmid and Wasserman.<sup>(10)</sup> There appeared to be several discontinuities, but, since our X-ray study was only a semi-quantitative survey of the aluminum-zinc system, the precision of the lattice measurements was not sufficient to locate the phase boundaries. The resolution in the X-ray patterns was not sufficient to record the dual phase structure in the beta plus gamma region which Owen and Iball<sup>(11)</sup> were able to show.

The difference in crystal structure between beta and gamma must be more obscure than the X-ray diffraction patterns can disclose. Perhaps there exists a difference in the electron configuration of the constituent atoms of beta and gamma, or a difference in the type of electron sharing between the atoms.

The actual mechanism of the atomic movements occurring during the beta decomposition has not been determined. Schwarz and Summa<sup>(8)</sup> regard the decomposition as an allotropic transformation. They say that zinc alloyed with aluminum exhibits a polymorphism otherwise suppressed. Thus zinc alloyed with aluminum exists as a face-centered cubic structure above the eutectoid temperature and below it as a hexagonal close-packed structure. They picture the transformation as taking place by the interplanar shifts hypothesized in the transformation between the allotropes of cobalt, thallium, silver iodide and zinc sulfide. Schwarz and Summa do not state by what mechanism the



gamma is formed when beta transforms to alpha; this would have to take place by the segregation of gamma from the alpha.

In the X-ray study of the aging of the beta containing magnesium as inhibitor, it was observed that the initially *coarse-grained beta* decomposed into *fine-grained alpha* and *coarse-grained gamma*. It appears as though the zinc-rich phase, alpha, segregates from the beta much as a phase separates from a supersaturated solid solution. The matrix beta crystal, depleted of its high zinc content, now becomes a gamma crystal with fine-grained alpha dispersed throughout the crystal.

This was also studied by Edmunds<sup>(7)</sup> in an excellently conducted series of experiments using the Laue method of crystal analysis, for the study of the decomposition of single crystals of beta. He noted that

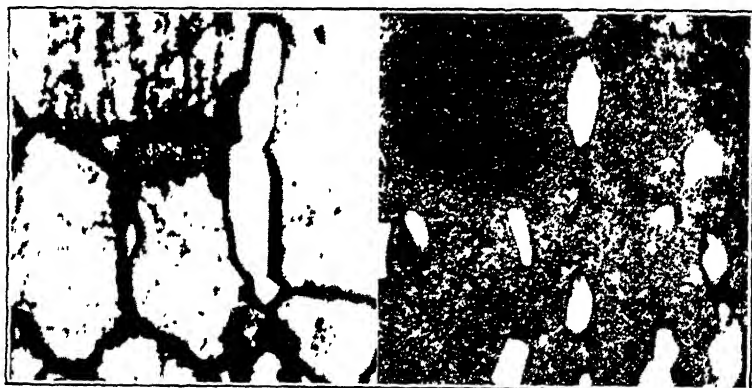


Fig. 3, three weeks aging.

Fig. 4, nine weeks aging.

FIGS. 3 AND 4.—ALUMINUM-ZINC ALLOYS QUENCHED FROM 325° C. AND ALLOWED TO AGE AT ROOM TEMPERATURE; 20 PER CENT ALUMINUM, 0.1 PER CENT MAGNESIUM.  $\times 1000$ .

Photomicrographs by J. L. Rodda.

the gamma crystals were in essentially the same orientation as the original beta crystal, and, further, that when the eutectoid was heated to the region of beta stability, the resultant beta crystals were very similar in orientation to the original beta grain. The alpha crystals were too fine grained to give rise to a Laue pattern.

This question of the mechanism of decomposition could be further elucidated if structures of the Widmanstätten type were developed and analyzed crystallographically. No attempts to do this have been made. Figs. 3 and 4 show the typical structure developed in the aging of beta containing the inhibitor magnesium, a structure too fine for crystallographic analysis.

The foregoing X-ray evidence on the relation of the eutectic to the parent beta crystals is not compatible with the previously quoted theory of Schwarz and Summa. By their theory the products of the decom-

position of coarse-grained beta would be coarse-grained alpha and fine-grained gamma, whereas the experimental evidence presented in this paper shows that the reverse is true.

### SUMMARY

The eutectoidal decomposition of the beta phase of the aluminum-zinc system has been studied with the purpose of determining the effect of this decomposition on the shrinkage occurring during the aging of zinc-alloy die castings. It has been found that the beta phase decomposes in less than one week of aging in die castings. This rapid decomposition takes place in spite of the copper and/or magnesium present in zinc-alloy die castings, whereas single-phase beta alloys containing magnesium require over six weeks for the complete decomposition to take place at room temperature.

The increase in density or shrinkage that accompanies the beta decomposition has been measured experimentally and found to be consistent with the shrinkage calculated from crystal-structure data. The possible influence of this shrinkage effect on the shrinkage occurring during the aging of zinc-alloy die castings is estimated and discussed.

It is shown that the beta decomposition cannot be the sole cause of the aging shrinkage in die castings. Other phase changes that contribute to the shrinkage phenomenon will be reported upon in later papers.

Additional data on the beta phase, primarily of fundamental interest, have been presented. These data consist of a measurement of the heat of decomposition, a study of the eutectoid temperature, and a discussion of the mechanism of the decomposition.

### ACKNOWLEDGMENT

The authors again acknowledge their appreciation to those of their colleagues in the Research Division, The New Jersey Zinc Co., whose contributions have been mentioned in the text of the paper and to other members of the Research Division who assisted during the investigation and in the preparation of the manuscript.

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## DISCUSSION

(W. H. Finkeldey presiding)

R. G. KENNEDY, JR., Cleveland, Ohio (written discussion).—This paper is interesting and instructive in its correlation of shrinkage in zinc-base die castings with the decomposition of the beta phase of the aluminum-zinc system. The authors are to be complimented on their technique for concentrating the beta and gamma phases in die castings so that X-ray patterns can be obtained from them.

In their notes on the calorimetric determination of the heat of decomposition of the beta phase the authors claim an accuracy of 3 per cent. I believe this accuracy could be increased somewhat by using a stable liquid other than water in the calorimeter vessel, since the pure beta alloy is attacked moderately when in contact with water.

With regard to Fig. 1, which shows the rise in temperature accompanying the beta decomposition, there is one point worthy of discussion. The authors quenched their specimens in water at room temperature and consequently the beta phase started to decompose immediately. Fraenkel, Hanson and Gayler and other investigators, including myself, have invariably found that the maximum heat evolution occurs 5 or 6 min. after quenching instead of  $1\frac{1}{4}$  min. as shown in Fig. 1. Had the authors quenched their specimens into ice water, better agreement between their results and those of other investigators would have been obtained.

A more important effect, however, on the time of decomposition of the beta phase is the presence of small amounts of impurities in the alloys. It would be interesting to know whether analyses have been carried out on the alloys listed in Table 1 for other elements than those shown. Many metallurgists have noted the retarding effect on the beta decomposition which is produced by additions of the order of 0.1 per cent or less. In my case I have found that, with a beta alloy containing 0.02 per cent total impurities, the time of decomposition after quenching in ice water and aging at room temperature was about  $5\frac{1}{2}$  min., but with an alloy made from commercially pure materials containing 0.8 per cent total impurities, the time of decomposition was about 12 min., or twice the time for the very pure alloy. Anderson has shown this retarding effect, which is apparent with copper additions and even more so with additions of magnesium. According to the authors, their alloys were made from materials containing 0.31 per cent total impurities (mostly in the aluminum) and this fact has undoubtedly caused the decomposition as shown by the shrinkage in a beta alloy containing 0.1 per cent magnesium (Fig. 2) to extend over a somewhat longer period of time than has been recorded by other investigators. Schwarz and Summa have shown by X-ray measurements that the beta phase decomposed practically in one week after quenching, even though the alloy contained 0.1 per cent magnesium. Putting their data at three weeks for complete decomposition of the beta phase gives a period of half that shown in the present paper. In this respect the authors have evidently misinterpreted my own paper. The beta alloy containing 0.21 per cent magnesium that I found showed very little shrinkage during the first four days after

quenching was examined by X-rays several weeks after the shrinkage measurements had been made, merely as a check to see whether the face-centered cubic structure of the beta phase had been preserved. It was found that the beta had decomposed and so the statement "0.21 per cent magnesium does not prevent the change  $\beta \rightarrow \alpha + \gamma$  from taking place at room temperature" is essentially correct. The great retarding effect of magnesium has been shown by several investigators, but a *permanent* cure (by additions to the alloy) for the shrinkage malady in zinc-base die castings has not been found. A method for permanently stabilizing the beta phase at or near room temperatures will be a welcome contribution to our knowledge of unstable phases in general.

M. L. FULLER AND R. L. WILCOX (written discussion).—Mr. Kennedy has correctly stated that the time of decomposition of the beta phase in the pure aluminum-zinc alloys would have been different from that reported if the quenching had been carried out at 0° C. instead of 20° C. It is to be expected that the observations of various investigators on the rate of decomposition of so unstable a phase as beta aluminum-zinc would differ from one another. Differences in the impurity content and in the experimental conditions greatly affect the phenomenon.

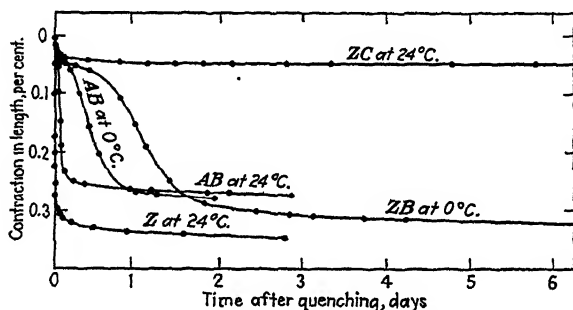


FIG. 5.—CONTRACTION CURVES SHOWING HOW LOWER AGING TEMPERATURES AND SMALL AMOUNTS OF MAGNESIUM RETARD THE SHRINKAGE AFTER QUENCHING.

Specimen Z has no magnesium, specimen ZB has 0.04 per cent Mg, and specimen ZC has 0.21 per cent Mg.

(R. G. Kennedy, Jr.: Fig. 15, *Metals & Alloys*, June, 1934.)

The paper primarily deals with zinc-alloy die castings, therefore it was only pertinent to determine the relative inhibiting effects of copper and magnesium in quenched single-phase beta alloys and to observe the extent to which this inhibiting action is effective in die castings.

With respect to the effect of the beta decomposition on the shrinkage in zinc-alloy die castings, the writers disagree with Mr. Kennedy. In Fig. 15 of the paper by Mr. Kennedy<sup>17</sup> (reproduced here as Fig. 5) alloys Z, ZB and ZC are alloys of the beta composition having 0.0, 0.04 and 0.21 per cent magnesium, respectively. It is shown in this figure that the shrinkage of alloy ZC is only about 0.04 per cent whereas the shrinkages in alloys ZB and Z are about 0.3 per cent. Mr. Kennedy concludes that the shrinkage is much smaller in the presence of magnesium in spite of an alleged beta decomposition in all three cases. Since Mr. Kennedy's X-ray examination was made "several weeks after the shrinkage measurements had been made," it was unwise to conclude that the beta of alloy ZC had decomposed completely with very little shrinkage. On the basis of these data Mr. Kennedy theorized that the shrinkage of only 0.04 per cent in alloy ZC was due to an expansion effect of the magnesium sufficient to compensate for the shrinkage effect of the beta decomposition. It seems evident from the shrinkage and X-ray data obtained with alloys 4458 and 4801

are written primarily from the casting point of view. For many years little authentic information was published on this subject, so each producer had to find his own solution to a given problem, while the consumer frequently had to choose between several conflicting recommendations with regard to the material for a given part. That this state of affairs prevailed not many years ago is well illustrated by a paper by Sam Tour<sup>1</sup>, in which he outlined certain of his own observations as to the effects of composition on the castability and properties of aluminum-base die castings.

In an attempt to clarify this situation and to make available to both producers and consumers the essential facts regarding die-casting alloys, a committee of the American Society for Testing Materials undertook the collection of available data and an investigation of the merits of the then commonly used alloys<sup>2</sup>. This work, although very extensive and not yet complete, has developed an excellent fund of authentic data illustrating the relations between nominal compositions and properties. Several writers have presented analyses of these data, among them D. L. Colwell<sup>3</sup> and A. J. Field<sup>4</sup>, who made brief studies of the effect of composition on properties.

It was believed, however, that there were still factors regarding corrosion resistance and effect of impurities which could profitably be investigated in order to establish a relatively sound basis for comparing the several alloys. Such an investigation obviously could become highly involved and quite extensive but in this case was limited to a study of only a few of the more widely used alloys. In this paper, the authors briefly outline the investigation, and offer for consideration the results that so far have been secured. It is hoped that the data presented will enable both producers and consumers to appreciate the effects of various elements on the properties and corrosion resistance, and to better analyze the relative merits of the more common aluminum-base die-casting alloys.

### SELECTION OF ALLOYS AND TEST SPECIMENS

Inquiry among the die-casters indicated that about six aluminum-base alloys, all covered by A.S.T.M. specifications<sup>5</sup>, enjoyed more than passing use. It was decided, therefore, that the nominal compositions of these

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<sup>1</sup> S. Tour: Aluminum Alloys for Pressure Die Castings. *Proc. Amer. Soc. Test. Mat.* (1929) **29**, pt. II, 487.

<sup>2</sup> *Proc. Amer. Soc. Test. Mat.* (1928) **28**, pt. I, 202 and succeeding volumes.

<sup>3</sup> D. L. Colwell: Effect of Composition on Aluminum-base Die-casting Alloys. *Proc. Amer. Soc. Test. Mat.* (1931) **31**, pt. I, 268.

<sup>4</sup> A. J. Field: The Physical Properties of Aluminum-Base Die-Casting Alloys. *Proc. Amer. Soc. Test. Mat.* (1932) pt. I, 285.

<sup>5</sup> B85-33T, *Proc. Amer. Soc. Test. Mat.* (1933) **33**, pt. I, 595, 641.

alloys, as indicated by the current specifications, should be employed in the tests. The alloys included several noted for their excellent castability, others that polished well, and one that employs secondary metal and is, therefore, under certain market conditions, of low cost; so covered the field reasonably well. In addition, to study the effects of the various impurities, one alloy was made in both nominal and high-purity grades while another was made in several grades, each having one impurity in appreciable amount.

For this investigation only two types of specimens were employed, the standard round tension specimen for die castings<sup>6</sup>, shown to give most uniform results by the A.S.T.M. tests, and a thin plate casting for which a die happened to be available. This casting was particularly suited for studying the effect of corrosion on surface appearance.

### PROCEDURE

There seems to be no point in expounding the minute details of the investigation, since no part of the procedure was new or unusual. A brief résumé, however, may be of some value when studying the results secured.

Briefly, the required specimens of the 14 compositions involved were cast under commercially controlled conditions. Three tension specimens and one plate were selected at random from the samples of each composition and were submitted for chemical analysis, after which all of the remaining tension specimens were radiographed. Samples shown by the radiographs to be either defective or of questionable quality were discarded and those remaining were classed as good, fair or poor. As five bars were to be used for each test, groups of five were then assembled from the three classes in proportion to the number of bars in each class; thus making each group an approximate cross-section of the entire lot.

After the specimens had been prepared they were exposed to the various corroding media: steam and paraffin, the 3.5 per cent salt (NaCl) spray, and five atmospheres (one industrial, one sea coast, one tropical and two industrial-sea coast locations). A group of five specimens of each alloy was used for each period of each exposure and a similar group was retained in the laboratories for determining the uncorroded properties. In addition, five specimens of each alloy, machined to accurate length, were exposed in each test to determine whether growth was induced by the exposure. Ten plate specimens, each with half of one side polished, were exposed in each test for observation of surface attack and appearance.

A definite period of aging between casting and exposure was employed for each alloy in all tests except the atmospheric exposures.

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<sup>6</sup> See *Proc. Amer. Soc. Test. Mat.* (1928) 28, pt. I, 203.

Metallographic examinations were made to check the type and depth of attack in corroded specimens and to study briefly the structures of several of the alloys.

### RESULTS AND DISCUSSION

In Table 1 are assembled the analyses of the various alloys as determined from the composite samples. In view of the method of sampling, it is believed that these results represent fairly well the average analysis of each material. Little need be said here about these analyses except to direct attention to the close control of impurities in alloys Vb to Vg and XIIa. Nickel, however, in alloy IX is approximately 3 per cent instead of the nominal 4 per cent.

TABLE 1.—*Analyses of Materials*

Alloy*	Nominal Composition, Per Cent	Composition <sup>b</sup> , Per Cent							
		Cu	Si	Fe	Ni	Zn	Mn	Mg	Others
IV	5 Si.....	0.39	4.78	1.55	0.36	0.42	0.25	0.05	
V	12 Si.....	0.42	11.83	1.50	0.23	0.43	0.21	0.02	
VI	2 Cu, 2 Si.....	1.90	2.82	1.52	0.29	0.43	0.24	0.05	
VII	4 Cu, 5 Si.....	3.90	4.85	1.27	0.18	0.30	0.30	0.04	
IX	4 Cu, 2 Si, 4 Ni.....	3.94	2.09	1.49	3.18	0.30	0.28	0.03	
Va	High-purity 12 Si.....	0.05	11.69	0.28	0.00	0.00	0.01	0.00	
Vb	Low-purity 12 Si.....	0.48	11.87	2.01	0.49	0.65	0.29	0.10	Pb 0.08
Vc	12 Si, high Ni.....	0.04	12.18	0.38	0.49	0.00	0.01	0.00	
Vd	12 Si, high Fe.....	0.04	11.87	3.15	0.01	0.00	0.02	0.00	
Ve <sub>12</sub>	12 Si, high Zn.....	0.04	11.76	0.33	0.00	1.29	0.01	0.00	
Vf	12 Si, high Cu.....	1.19	11.75	0.31	0.00	0.00	0.01	0.00	
Vg	12 Si, high Sn.....	0.04	11.71	0.31	0.00	0.00	0.01	0.00	Sn 0.46
XIIa	High-purity 8 Cu, 3 Si.....	7.81	3.09	0.46	0.00	0.00	0.00	0.00	
XIIb	8 Cu, 3 Si.....	7.81	3.07	2.43	0.45	1.39	0.30	0.08	

\* A.S.T.M. Specifications B85-33T, *Proc. A.S.T.M.* 33, pt. I, 595, 641.

<sup>b</sup> Composite samples from three specimens of each alloy chosen at random. Aluminum-balance.

The mechanical properties included in Table 2 represent in each case the average of five tests made 12, 26 and 46 weeks after casting. Since a study of the radiographs indicated that the porosity present was about typical of that generally found in die castings and that, at its maximum, probably had little effect on properties, it is believed safe to attribute most variations in properties to composition. It must be kept in mind, however, that the inherent variation among the specimens as well as the numerous difficultly controlled factors in the casting process may induce changes in properties greater than small changes in composition.

Inasmuch as the previously cited literature and the data of A.S.T.M. Committee B-6 thoroughly examine the relations between the nominal compositions and mechanical properties, little reference to these relations

TABLE 2.—Room-temperature Aging of Aluminum Die-casting Alloys

Alloy <sup>a</sup>	Weeks after Casting				12			26			46		
	Nominal Composition, Per Cent				Tensile Strength, Lb. per Sq. in.	Yield Strength, Lb. per Sq. in.	Elongation, Per Cent in 2 in.	Tensile Strength, Lb. per Sq. in.	Yield Strength, Lb. per Sq. in.	Elongation, Per Cent in 2 in.	Tensile Strength, Lb. per Sq. in.	Yield Strength, Lb. per Sq. in.	Elongation, Per Cent in 2 in.
IV	5 Si.....				26,780	12,700	4.6	27,335	12,200	3.7	29,270	12,550	4.3
V	12 Si.....				33,465	17,200	1.8	34,070	18,150	2.0	36,640	18,800	2.0
VI	2 Cu, 2 Si.....				29,985	13,600	4.5	29,550	14,600	4.1	31,390	14,450	4.3
VII	4 Cu, 5 Si.....				36,075	19,100	2.8	35,540	20,300	2.6	34,980	19,650	2.7
IX	4 Cu, 2 Si, 4 Ni.....				33,200	20,100	2.0	33,580	21,500	1.6	34,670	21,400	1.9
Va	High-purity 12 Si.....				33,670	16,060	4.1	33,860	15,260	4.5	32,970	15,450	3.9
Vb	Low-purity 12 Si.....				30,320	20,150	1.2	30,445	20,760	0.9	31,680	21,900	1.0
Vc	12 Si, high Ni.....				34,440	16,700	4.0	33,540	14,850	3.7	33,880	15,750	3.6
Vd	12 Si, high Fe.....				26,435	19,200	1.0	26,480	18,350	0.6	28,200	19,800	0.8
Ve	12 Si, high Zn.....				32,390	14,650	4.2	32,780	16,600	4.5	33,240	15,500	3.7
Vf	12 Si, high Cu.....				36,205	17,950	3.5	35,475	16,500	3.2	37,975	18,150	3.7
Vg	12 Si, high Sn.....				28,790	14,750	2.6	28,565	14,700	3.2	29,960	14,650	3.2
XIIa	High-purity 8 Cu, 3 Si.....				28,520	19,200	1.5	29,980	22,160	1.5	29,900	22,145	1.6
XIIb	8 Cu, 3 Si.....				36,515	27,800	1.1	36,335	29,900	1.0	37,525	30,150	1.5

<sup>a</sup> See Table 1, note a



need be made here except to remark that the present tests essentially confirm those previously reported. In considering the effect of the impurities in the 12 per cent silicon alloy, it should be remembered that only one percentage, representing the maximum to be expected in ordinary die-casting practice, was employed, and therefore the effect of progressive additions or the combined effect of several impurities was not studied. Tin, in this alloy, markedly reduces the mechanical properties, while nickel and zinc have little effect. Copper, as would be expected, raises the strength and lowers the elongation. The high iron has reduced the elongation and, to some extent, the tensile strength. It is common experience that iron, in the amounts ordinarily encountered in die-casting practice, reduces the elongation, but not the tensile strength.

The greater strength of the 8 per cent copper, 3 per cent silicon (XII) alloy of nominal purity over that of the high-purity composition is probably the result of the higher total of the alloying constituents and the somewhat smaller amount of porosity.

Owing to the unavoidable delay between casting the specimens and the determination of their mechanical properties, no information was obtained on the effect of the early period of room-temperature aging on mechanical properties. Tests made 12, 26 and 46 weeks after casting (Table 2) indicate essentially no changes in properties greater than might be induced by variations within a group of specimens. Since room-temperature aging of as-cast aluminum alloys proceeds very slowly, if at all, these data indicate that no changes of commercial importance occurred during the first 12 weeks of aging.

The A.S.T.M. specifications for zinc-base die castings include, as an optional acceptance test, exposures for 10 days to steam at 95° C. The effect of this test on aluminum-base alloys is frequently a subject of question, so it was believed desirable to conduct such a test. In order to segregate the changes caused by temperature alone from any that might be induced by steam corrosion, duplicate specimens were exposed in a paraffin bath at the same temperature, a procedure used in the investigational work of Committee B-6, A.S.T.M. These exposures, therefore, served essentially as two tests: (1) a study of elevated-temperature aging, and (2) a steam corrosion test. An examination of the changes in tensile strength (Table 3) leads to the general conclusion that the elevated temperature has not induced aging in any of the alloys except the 8 per cent copper, 3 per cent silicon alloy (XIIa and b) and possibly the high-tin 12 per cent silicon alloy (Vg). Nor has the presence of steam at this temperature caused any corrosion. In nearly all cases, the changes in tensile strength were of the order of 4 to 6 per cent, which is of less magnitude than might be encountered between two bars.

These tests also presented an opportunity for studying the growth characteristics of aluminum die-casting alloys, a factor that apparently

TABLE 3.—*Effect of Exposure at 100° C. on the Mechanical Properties*

Alloy <sup>a</sup>	Original Properties			Change from Exposure, Per Cent											
	Tensile Strength, Lib. per Sq. In.	Yield Strength, Lib. per Sq. In.	Elongation, Per Cent in 2 In.	10 Days			20 Days			40 Days					
				Tensile Strength	Yield Strength	Elongation	Tensile Strength	Yield Strength	Elongation	Tensile Strength	Yield Strength	Elongation			
IV	29,780	12,700	4.6	-3.3	7.1	-10.9	5.4	+11.8	-26.1	2.0	+19.7	-23.9			
A	33,465	17,200	1.8	-4.0	6.7	-15.2	-4.1	+13.0	-10.6	2.1	+16.5	-23.9			
V	29,985	13,600	4.5	+0.2	5.8	-5.6	-2.6	+7.9	-5.6	+7.8	+20.6	0			
VI	36,075	19,100	2.8	+1.5	7.7	+6.7	-4.8	+13.2	-11.1	+4.8	+22.1	-16.6			
VII	33,200	20,100	2.0	-4.2	3.7	+2.2	-1.7	+2.1	-7.1	+2.4	+8.9	-11.1			
A	33,670	15,050	4.1	-3.5	2.1	+10.7	-6.2	0	-7.1	-3.1	+7.6	+3.8			
IX	30,320	20,150	1.2	-3.0	0.5	-25.0	2.0	+5.2	-20.0	+6.5	+10.4	-25.0			
Va	34,440	18,700	4.0	-0.2	4.1	-11.1	1.0	+3.0	-3.1	+1.3	+9.6	-9.5			
Vb	26,435	14,650	4.2	-0.2	6.1	-16.7	2.2	+4.3	-3.1	-2.2	+10.0	-8.0			
Vc	32,390	17,950	3.5	+0.5	9.9	-25.0	3.1	+12.7	-25.0	+2.4	+18.1	-25.0			
Vd	28,790	14,750	2.6	-0.9	3.8	-22.5	1.8	+13.9	-17.5	+1.5	+15.4	-19.7			
VIa	28,620	19,200	1.5	-0.9	2.6	-20.0	5.7	0	-12.5	-2.3	+8.4	-7.5			
VIb	36,615	27,800	1.1	+2.8	0.8	0	+1.6	+4.9	0	+2.1	+6.0	-10.0			
VIIa				+6.7	5.1	0	-0.9	+5.2	-9.5	+4.9	+3.4	0			
VIIb				+0.7	11.9	-4.8	-2.7	+10.6	-2.9	+1.7	+9.0	-10.6			
VIIIa				+1.6	3.1	+2.9	1.0	+6.8	0	0.2	+7.5	-14.3			
VIIIb				+0.8	2.5	+26.9	1.7	+8.1	-16.4	1.9	+9.7	+7.7			
IXa				+9.1	6.8	+11.5	6.1	+12.3	+11.3	+7.2	+30.2	+11.5			
IXb				+8.3	16.9	-13.3	9.7	+18.3	-11.3	+4.5	+23.7	-20.0			
XIa				+2.5	15.1	-26.7	14.4	+22.1	-24.7	+10.1	+26.0	-9.1			
XIb				+2.3	15.6	-26.1	9.0	+22.9	-18.2	+6.8	+11.9	-9.1			
XIIa				-4.0	4.5	-9.1	1.8	+0.4	-9.1	+4.5	+14.7	-9.1			
XIIb				0	2.5	-	1.6	-0.7	-	-	-	-			

\* See Table 1, note a. \* Five specimens were tested for each period and type of exposure.

<sup>b</sup> A—Exposed in steam.

B—Exposed in paraffin.

has not previously been subject to laboratory investigation. Commercial experience, however, offered reasonable assurance that any growth that might be found would be more of academic than of practical importance. For this work, standard tension specimens with the ends machined to planes normal to the axis of the specimen were employed. Five bars of each alloy were exposed in steam and a like number in paraffin and their lengths determined at frequent intervals. The average unit change in length of the bars was computed for each period and is included in Table 4. These data show that, as at higher temperatures, a definite amount of growth is induced by exposures at 100° C. but that the actual unit growth is of a very small order. Further, from the fact that the growths in both steam and paraffin are much the same for most of the alloys, it appears that the phenomenon is essentially a temperature effect and bears no relation to steam corrosion. In connec-

TABLE 4.—Unit Growth<sup>a</sup> of Aluminum Die Castings<sup>b</sup> Exposed to Steam and Paraffin at 100° Centigrade

Alloy <sup>c</sup>	10 Days		20 Days		40 Days		60 Days		80 Days		100 Days	
	Steam	Para- fin	Steam	Para- fin	Steam	Para- fin	Steam	Para- fin	Steam	Para- fin	Steam	Para- fin
IV	2.2	-0.5	3.3	0	7.4	3.8	15.6	7.4	16.7	10.7	16.9	12.0
V	2.0	2.0	3.1	2.7	7.8	8.2	12.3	12.5	17.1	18.5	17.7	19.4
VI	4.2	2.5	5.9	3.2	10.3	9.6	15.5	15.9	19.9	19.6	20.1	19.6
VII	3.8	2.0	4.1	1.3	7.1	3.8	12.0	7.6	16.2	13.8	19.1	17.9
IX	6.5	5.4	9.3	7.8	11.3	10.5	15.1	14.3	19.1	19.0	21.8	21.2
Va	4.0	11.8	6.0	13.6	8.7	17.6	12.1	21.2	17.4	25.0	17.6	26.1
Vb	3.8	3.3	6.9	7.1	8.7	8.9	14.3	13.8	18.5	17.8	18.9	21.4
Vc	0	1.6	2.7	3.1	13.4	6.7	18.1	10.5	20.8	13.6	21.0	16.3
Vd	-0.7	-3.3	0.2	-2.5	6.9	0.2	10.0	3.1	11.8	4.7	10.7	5.8
Ve	1.3	2.8	4.5	5.6	13.6	8.4	17.4	11.5	17.9	16.2	17.9	17.3
Vf	8.2	10.5	10.0	13.6	23.4	16.5	28.3	21.4	31.9	26.8	33.4	30.4
Vg	5.8	15.4	8.2	21.0	33.4	29.7	38.6	36.8	42.1	43.6	44.6	46.3
XIIa	-2.5	-2.2	0.4	0.8	2.4	1.8	6.9	2.2	9.5	6.7	10.2	9.2
XIIb	1.8	2.2	3.8	3.1	10.2	9.1	20.5	15.6	30.1	25.8	36.6	30.3

<sup>a</sup> Times 10<sup>-6</sup> (=0.00001).

<sup>b</sup> Bars 9 in. long used for tests.

<sup>c</sup> See Table 1, note a.

tion with a study of the growth data, the matter of minor changes in room temperature at the times that the various measurements were made must be kept in mind. Unfortunately, no "constant-temperature" room was available for the measurements and slight variations were unavoidable. For instance, the expansion obtained in the usual 10-day test in either steam or paraffin is in the same range as that which would be produced by a 2° C. increase in temperature. Even after 100 days in either steam or paraffin the changes are too small to be of practical significance. These data under laboratory controlled conditions should

serve to allay the fears of some potential users of die castings who fail to differentiate between the various die-casting alloys.

Growth in aluminum alloys is generally conceded to result from the precipitation of alloying constituents from a supersaturated solid solution. Since die castings are inherently a rapidly chilled product and in most cases contain alloying elements in amounts exceeding the low-temperature solubilities, it is to be expected that growth would occur. Studies of growth at higher temperatures have been rather extensive, in connection with permanent mold castings, and have fairly well established that, in time, a certain maximum growth will be attained at any temperature. At a lower temperature, this same principle should apply but the required period for reaching the maximum should be relatively longer. However, in uses at elevated temperatures where even this small growth is undesirable, a low-temperature annealing treatment can be applied.

Atmospheric exposure tests, of course, have not yet given any results and probably will not produce much information of interest in less than two to four years. The salt-spray tests, however, are of a much more severe nature and already have produced some interesting comparisons. These comparisons are graphically illustrated in Fig. 1, which shows the percentage of losses in tensile strength of the various alloys after exposures of 12 and 26 weeks. It is believed that these losses are most suitable as criteria of resistance to this type of corrosion in that, for some alloys, the attack is so limited that losses in yield strength are too small to be significant while in all alloys the original elongation is too low to justify a computation of the percentage change.

For preparing Fig. 1, the alloys were arranged from left to right in what is believed to be a decreasing resistance to salt-spray corrosion. To accomplish this, the changes in strength after each period were considered and an average order of merit determined. Although this method produces some inconsistencies in the two periods, it has the advantage of definitely illustrating what alloys may be subject to such variations and of offering a more concrete analysis of relative merits.

While studying the chart, two important factors should be kept in mind: The severity of the test, and the inherent variation in specimens. The salt spray is an accelerated laboratory test and, like most accelerated tests, is most suitable only for comparing alloys of the same metal base. It is not especially suited for comparing dissimilar metals, nor are the losses in properties, in themselves, of anything but comparative significance. The important difference between the salt-spray test and marine exposures in service is that in the service exposures the frequent periods of drying serve to build up a highly resistant protective scale. An analysis of these data must also take into consideration that a change of up to 10 per cent may easily be introduced by variations in die-cast specimens. With this in mind, it is believed safe to conclude that the

several better alloys in the tests are essentially unattacked after even 26 weeks exposure while the choice between two alloys whose losses vary but a few per cent becomes a matter of personal preference or commercial expediency.

In general, the illustration clearly shows the deleterious effect of copper on the corrosion resistance of aluminum die castings; as evidenced by the superiority of alloy Va over alloy Vf and of alloy IV over alloys VI, VII, IX and XII. Like copper, tin is obviously undesirable in materials

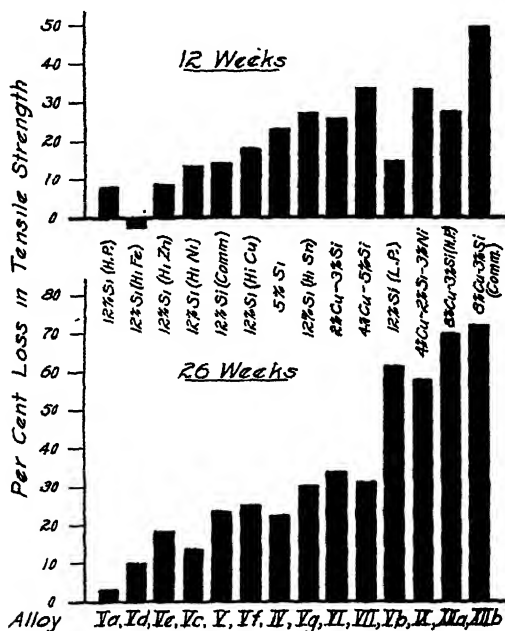


FIG. 1.—EFFECT OF EXPOSURE TO THE 3.5 PER CENT SALT SPRAY ON THE TENSILE STRENGTH OF DIE-CAST TEST BARS.

subject to corrosive conditions, but nickel and zinc probably can be tolerated in reasonable quantities.

A periodic visual examination of the plate samples exposed to the salt spray furnished interesting supplementary information in relation to the tensile test results. In general the visual examination placed the alloys in the same relative order as the shorter period (12 weeks) of the tensile test results. It is interesting in this connection to note that in the early stages of corrosion the copper-silicon-nickel alloy (No. IX) preserved a better appearance than the two copper-silicon alloys without nickel (No. VI and No. VII), but that after longer periods of exposure the nickel-bearing alloy developed a few relatively deep pits which caused a marked lowering in the tensile strength, as illustrated by the 26 weeks data. The surface appearance of the plates of the low-purity 12 per cent

silicon alloy (Vb) did not justify the low rating given this alloy in Fig. 1 and it is perhaps significant that the losses after 12 weeks are also relatively low. Again, in the early stages of corrosion the high-iron 12 per cent silicon alloy (Vd) showed less corrosion of the surface than the high-purity 12 per cent silicon alloy (Va) although after 26 weeks the tensile losses on the high-iron alloy are slightly greater than in the high-purity alloy. The fact that the iron content of this alloy is markedly above the usual commercial range should not be overlooked.

These observations also illustrate a difficulty often encountered in corrosion testing where the relative corrosion resistance of several alloys seems to vary with the length of the corrosion period. In general, it seems desirable to select a corrosion period in which the most resistant alloys are only slightly attacked and the less resistant alloys have tensile losses of considerable magnitude. This was about the condition obtained in the 12 weeks test. The fact, however, that certain of these alloys showed disproportionate losses in the longer period may illustrate an inherently lower corrosion resistance and suggest that possibly the good showing in the early stages of the test was the result of an unusually heavy or protective surface film.

### CONCLUSIONS

An analysis of the results now available from the more accelerated tests of this investigation lead to the following important conclusions:

1. That it is possible to produce aluminum-alloy die castings of superior corrosion resistance to those heretofore produced by the control of impurities in the 12 per cent silicon alloy within commercially obtainable limits.

2. The aluminum-silicon alloys are definitely more corrosion resistant than those containing appreciable amounts of copper. The corrosion resistance decreases with increase in copper.

3. The maximum impurities allowed by the A.S.T.M. specification for the 12 per cent silicon alloy permit an alloy composition of definitely inferior corrosion resistance, should all of the impurities reach the maximum coincidentally.

4. All the common impurities in the 12 per cent silicon alloy, except iron, at least slightly affect the corrosion resistance, copper and tin appearing most undesirable. It is particularly fortunate that iron, the least controllable impurity in die castings, has no detrimental effect on the corrosion resistance within the maximum range likely to be encountered.

5. Within the limits employed in the alloys studied, nickel and zinc appear not to affect the mechanical properties of the high-silicon alloy. Copper increases the strength and reduces the elongation, iron reduces the elongation and, if excessively high, may reduce the tensile strength, while tin lowers both strength and elongation.

6. No significant change in mechanical properties was found between 12 weeks and 46 weeks room-temperature aging. The aging induced by 40 days exposure at 100° C. in either steam or paraffin has resulted in no changes in tensile strength greater than 4 to 6 per cent, a change of less magnitude than might be encountered between two bars. No corrosive effect was noted from this period of exposure in steam.

7. The maximum unit growth obtained after 100 days in either steam or paraffin at 100° C. was between 0.00005 and 0.00046. The average growth obtained in a period of 10 days, the limit in the A.S.T.M. specifications test, was less than would result from an increase of about 2° C. in temperature during measurement. Except in the case of tin and perhaps copper in the high-silicon alloy, the composition does not affect the growth at 100° C.

## DISCUSSION

*(W. H. Finkeldey presiding)*

D. BASCH,\* Schenectady, N. Y. (written discussion).—This article apparently is in the nature of a progress report on a very interesting investigation, and parallels work done by A.S.T.M. Committee B-6 on 5 per cent and 12 per cent silicon alloy with controlled impurities. We are naturally greatly interested in this investigation but, of course, a broad interpretation and application of the results will have to wait on the atmospheric exposures which are now under way.

We thoroughly believe that the salt-spray test has only a limited usefulness, in that it does not cover industrial atmospheres and not even marine exposure where mixed with industrial atmospheres.

E. H. DRX, JR. (written discussion).—It would be more correct to say that the work of the A.S.T.M. Committee B-6 on 5 and 12 per cent silicon alloys with controlled impurities is the direct result of the work reported upon by Mr. Bowman and myself.

D. L. COLWELL,† Chicago, Ill. (written discussion).—The authors have successfully endeavored to substantiate certain opinions now held by those familiar with aluminum alloys concerning the effects of composition of aluminum die-casting alloys on certain properties. As they point out, progressive additions of impurities were not made. The data presented, however, seem to indicate conclusively that in most of the specimens studied the effects of the added impurities were so slight as to be of relatively little importance, and further studies of compositions with intermediate amounts of impurities would be useless effort. Several comments based on previous experience with these alloys and the uses to which they are commercially put may be of interest:

1. As stated by the authors, the effect of the steam and high-temperature paraffin aging is negligible. The greatest dimensional change given is less than 0.0005 in. in a 9-in. length, and this might well be due to variations in measurement conditions, as pointed out. Why, then, bother with this test? Many users of die castings still believe that in some mysterious manner the die-casting process imparts an instability to materials that otherwise are perfectly sound. It becomes periodically necessary,

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\*Schenectady Works Laboratory, General Electric Co.

† Metallurgist, Stewart Die Casting Corporation.

therefore, to point out that this instability was due to the material used at the time, and not to the process. The aluminum-base alloys specified by the A.S.T.M. and discussed by the authors are not and never were subject to this instability, and the data given in Tables 3 and 4 certainly offer ample proof of this fact.

2. The use of the tensile test for the valuation of the alloys is to be regretted, as the impact test as used by the A.S.T.M. is not only more sensitive but more nearly approaches the stresses generally encountered in service.

3. The tensile strengths given in Table 2 for alloys Vd and Vg are undoubtedly due to effects of casting conditions rather than of impurities. The extremely high iron content of Vd would cause great casting difficulty, but would increase rather than decrease the tensile strength.

4. Alloys XIIa and XIIb would have been more nearly representative with 7 per cent copper than with 8 per cent. The higher copper content is a hangover from the days of low silicon in this alloy.

5. The corrosion data indicate that copper is the most harmful ingredient in these alloys from a corrosion standpoint. In an alloy such as XII, the copper content makes it generally unsuited for corrosion resistance, and impurities are of relatively little importance.

6. Conclusions 1, 3 and 4 hardly appear justified from the data presented. If the 12-week salt-spray test is not severe enough to differentiate between the various high-silicon alloys tested (except for high iron and high tin, the former of which is probably due to other causes) any of these alloys would be amply resistant to the usual service. If the service expected approximates six months in 20 per cent salt spray, special tests should be devised.

J. J. BOWMAN AND E. H. DIX, JR. (written discussion).—The authors greatly appreciate Mr. Colwell's comments but on several points cannot fully agree with him; namely, comments 2, 3 and 6.

The choice between impact and tension test data for comparing aluminum die castings seems to the authors to depend at least as much upon the personal preference of and equipment available to the investigator as upon the relative merits of the tests. It must be granted, of course, that impact loading is frequently encountered in service and therefore such data might at times be of value in choosing materials. The authors hesitate to believe, however, that impact rather than tension loads are the rule and are also quite uncertain, because of the marked disagreement among the testing engineers, as to the real value of the impact test as a criterion of a material's resistance to suddenly applied loads.

The authors were of the opinion that the tension test, so widely used in the aluminum industry, would furnish most, if not all, of the information necessary to compare their materials and that the limited additional information secured from impact tests did not justify the added expense. This opinion resulted partly from a study of the impact test, per se, and of the relation of the data secured from it in other investigations with those resulting from tension tests.

Impact-test results are in general related to the elongations of the specimens and, for comparative purposes at least, offer no comparisons not determinable from elongation values. This was shown in a paper<sup>7</sup> presented some years ago by one of the authors and can be confirmed by comparing the results of arranging a series of die-casting alloys in order of descending impact strengths or elongations: the relative order will be found essentially the same in both cases. Of course, evaluating a series of alloys on the basis of elongation (or impact) results will produce a radically different

<sup>7</sup> E. H. Dix, Jr.: Charpy Impact Test as Applied to Aluminum Alloys. *Trans. A.I.M.E.* (1920) 64, 466.



arrangement than when tensile strength is used and the one employed probably would depend on the characteristic of the several alloys of immediate interest.

When analyzing the effects of corrosion (the principal purpose of this investigation), percentage change in mechanical properties is the criterion commonly used for aluminum alloys. For these analyses, tensile-strength data are the most suitable because the values are of such an order that relatively small variations in corrosion attack are not magnified into staggering variations in percentage changes. With impact or elongation values of the usual magnitude, however, small variations in the actual value—perhaps unimportant in themselves—may become percentage changes of a size wholly misleading. The latter properties, in addition, are also subject to erratic changes induced by variations in the material or by the limitations of the test. In general, then, the authors believe that the omission of the impact test has not resulted in a serious deficiency in the data and that the analyses of corrosion resistance based on percentage change in tensile strength are substantially dependable.

The authors' disagreement with Mr. Colwell's third comment is possibly essentially one of personal opinion. The relatively low tensile strengths of alloys Vd and Vg have been repeated throughout a number of mechanical property tests (room-temperature aging) and indicate that, regardless of whether they result from casting conditions or the added impurities, they are at least consistent in the entire set of specimens. The authors have interpreted these results to mean that iron or tin in the amounts present in these samples may reduce the tensile strength either by a direct effect or by introducing casting characteristics difficult or impossible of elimination. Since all of the specimens for this investigation were produced with one machine and under careful supervision, it is believed relatively safe to assume that variations may be ascribed to composition.

Comment 6 leads the authors to suspect that their close association with the tests and their attempt to present a paper of reasonable length has resulted in a failure to include sufficient data or to present the data used with the necessary clarity and force. They have no hesitation in reiterating their conclusion that the control of the minor impurities in the 12 per cent silicon alloy will result in a material with superior corrosion resistance. The tensile data and both microscopic and visual examinations sustain this conclusion. Admittedly the 12-weeks and 26-weeks salt-spray tests are extremely severe exposures, chiefly of value for rapid comparisons of similar materials (alloys of the same base) and not as well suited for estimating service life in most atmospheres as many special tests might be. There are many cases, however, where conditions approaching those of the salt spray may exist, and the results of such a test are a real guide. When the exposure conditions are markedly less severe, there is probably no economic justification for the use of an alloy superior to the present commercial 12 per cent silicon alloy.

## Die-casting of Brass

BY JOHN R. FREEMAN, JR., \* MEMBER A.I.M.E.

(New York Meeting, October, 1934)

THIS paper relates entirely to the casting of brass under fluid pressure in steel dies. Die castings of metals and alloys of low melting point have been available for many years but the development of brass die castings has been relatively recent, occurring within the past five years.

The successful development of brass die castings has resulted from the availability of alloy steels that would give satisfactory life as dies and the development of suitable die-casting machines.

The melting point of copper is 1084° C. (1983° F.) and of a high brass about 900° C. (1652° F.), as compared to 327.5° C. (621.5° F.) for lead, 419.4° C. (786.7° F.) for zinc and 658.7° C. (1217.7° F.) for aluminum, temperatures that are indicative of the casting temperatures required for the various types of alloys, of which the melting points are somewhat lower than those of the pure metals.

### TYPE OF DIE-CASTING MACHINE

In the well-known plunger and gooseneck types of die-casting machines used for casting the alloys of relatively lower melting point, much of the working mechanism is immersed in the molten alloy. For alloys having the relatively high melting point of brass, this obviously is impossible. Machines with a separate melting chamber are essential. Two rather distinct types are in extensive use at the present time, the Pack and Polak machines, the former designed by Charles Pack and developed at the American Brass Co., the latter developed by Joseph Polak, of Prague, Czechoslovakia.

The principles of operation of these machines have been described in articles by Pack<sup>1,2,3</sup> and by Sieg.<sup>4</sup>

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\* Technical Department, American Brass Co., Waterbury, Conn.

<sup>1</sup> C. Pack: Die Cast Metals for Automotive Use. Symposium on Developments in Automotive Materials A.S.T.M., March 19, 1930.

<sup>2</sup> Press Casting. *Metals & Alloys* (February, 1932).

<sup>3</sup> C. Pack: Press Casting Brass and Other Copper Base Alloys. *Metal Ind.* (May, 1934) 155; (June, 1934) 199.

<sup>4</sup> W. W. Sieg: Brass Pressure Castings Are Produced Economically. *Iron Age* (Nov., 1933).

For both types of machines the metal to be cast is maintained at proper casting temperature in a "holding pot," from which it is ladled in required amounts into the "cup" or pressure chamber of the die-casting machine. The difference in principle of operation of the two types of machines is illustrated in Figs. 1 and 2.

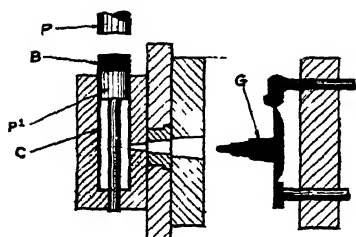
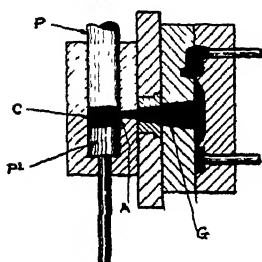
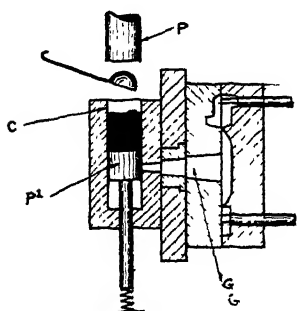


FIG. 1.—CASTING PRINCIPLE OF POLAK MACHINE. (FROM *Metal Industry*.)

In the cup of the Polak machine there are two pistons or plungers, the upper one of which ( $P$ ) moves downward to force the metal through the gate  $G$  into the die, and the lower one,  $P^1$ , after filling of the die acts upward, cutting off the excess metal from the gate and ejecting the slug from the cup. The gate is ejected with the casting from the die.

In the cup of the Pack machine (Fig. 2) there is but one plunger,  $P$ , which forms the bottom of the cup. The upper die is constructed so that when closed it covers the top

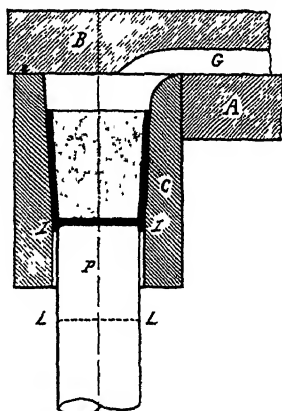


FIG. 2.—CASTING PRINCIPLE OF PACK MACHINE. (FROM *Metal Industry*.)

of the cup and also forms a gate into the die. An upward motion of the piston forces any metal in the cup into the die cavity. The entire gate remains attached to the casting. This is evident in Fig. 3, which shows a completed casting of standard test bars as ejected from the dies.

The type of cup used in the Polak machine requires certain characteristics in the metal to be cast. Liquid metal cannot readily be used. The metal is preferably cast therefore in a semi-molten or plastic condition by holding it at a suitable temperature between the solidus and liquidus; that is, in a partially molten condition. In this condition

the alloy can be ladled out of the holding pot, rolled up in the ladle to an appearance much like a meat ball and then dropped into the cup.

The term *Pressguss* (press casting) was originally applied to die castings made in this manner. To a certain degree it can be considered as intermediate between an extrusion and true die-casting operation.

In the Pack machine either liquid or plastic metal may be used, liquid metal when poured into the cup chilling sufficiently to form its own container, as indicated by the heavily shaded area in Fig. 2.

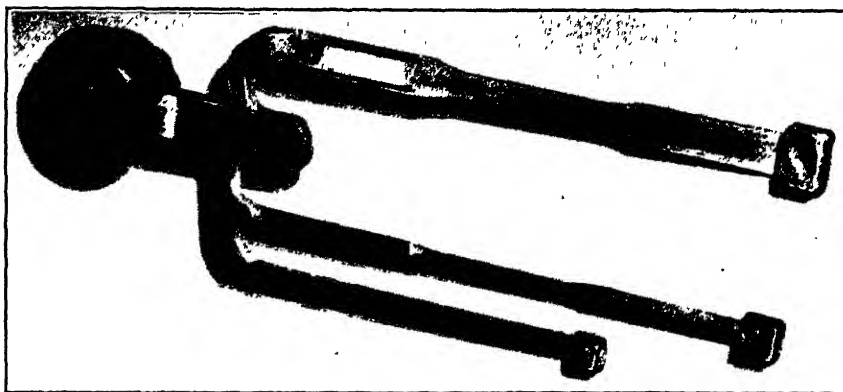


FIG. 3.—METHOD OF GATING IN PACK MACHINE, SHOWING STANDARD A.S.T.M. TEST BARS AS CAST ATTACHED TO GATE AND SLUG.

### BRASS DIE-CASTING ALLOYS

The alloys that may be die-cast commercially in either of the two types of machines are limited only by melting point and consequent casting temperature required.

At the present time the higher melting-point alloys cannot be die-cast because of limitations of die steels available. Alloys for use in the Polak machine are also limited to compositions having an appreciable plastic range. Pure metals and alloys with a narrow temperature interval between the liquidus and solidus, therefore, are not readily cast in the Polak machine.

The ability to cast an alloy in the plastic condition has a distinct advantage, however, in permitting casting at a lower temperature with consequent saving of die life.

Brass of composition 60 per cent copper and 40 per cent zinc has the lowest melting point of the commercial brasses, and for this reason is the most widely used for manufacture of brass die castings. Other elements, however, are added to obtain certain characteristics more or less peculiar to the die-casting process. The plastic range of the high brasses is quite narrow but may be greatly increased by the addition

of a small percentage of lead, owing to the immiscibility of lead in the molten condition in the brass alloy. For satisfactory operation in the Polak machine a minimum of about 0.5 per cent is required. Lead also, as is well known, confers machinability upon brass. It markedly reduces the ductility and in excess introduces hot shortness.

In the die-casting process the metal obviously must be maintained for appreciable periods at casting temperature in the holding pot, where it is uncovered and subject to continual oxidation by the atmosphere.

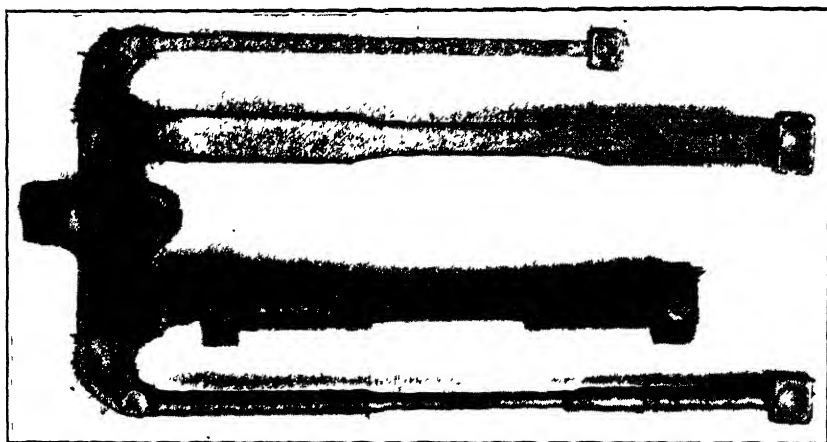


FIG. 4.—METHOD OF CASTING BRASS TEST BARS.

In the plastic or “mushy” state the oxide formed is not readily skimmed from the surface. The addition of about 0.1 to 0.2 per cent of aluminum has been found to inhibit this oxidation and apparently is generally used both in European and American practice. The aluminum also reduces the vaporization of zinc in the holding pot and diminishes the deposit of zinc oxide on the die surfaces. Tin is also added. This gives increased fluidity to the alloy in the casting, tends to inhibit segregation of lead in the holding pot when semiplastic metal is being used and increases the corrosion resistance of the final casting.

The alloy found most suited for general die-casting purposes in both types of machines has the following nominal composition: 60 per cent copper, 1 per cent tin, 1 per cent lead, remainder zinc and will contain in addition about 0.10 per cent aluminum. It has the following minimum physical properties: tensile strength 55,000 lb. per sq. in.; elongation, 9 per cent in 2 inches.

In addition to the common brasses, certain high-silicon alloys have been found eminently suited for die castings, having low melting point, about 900° C., good fluidity and unusually high strength. The nominal

composition of a very satisfactory alloy of this type<sup>5</sup> is 81.50 per cent copper, 4.25 per cent silicon, 0.15 per cent manganese, remainder zinc, and the minimum physical properties are: tensile strength, 85,000 lb. per sq. in.; elongation, 8.0 per cent in 2 inches.

The results of some tests to determine the effect of section and of lead content on brass die castings are given in Table 1. The test bars were cast in the Pack machine, as shown in Fig. 4. The small test bars were in accordance with recommended practice of the Committee on Die Casting of the A.S.T.M. The larger diameter (0.505 in.) test bar

TABLE 1.—*Effect of Section and of Lead Content on Brass Die Castings*

Alloy No.	Composition, Per Cent					Physical Properties							
	Copper	Tin	Lead	Aluminum	Zinc by Difference	Tensile Strength, Lb. per Sq. In.			Elongation, Per Cent in 2 In.			Charpy Impact, Ft.-lb.	
						Flat $\frac{7}{8} \times \frac{1}{2}$ in.	Round $\frac{1}{4}$ in. dia.	Round $\frac{3}{4}$ in. dia.	Flat $\frac{7}{8} \times \frac{1}{2}$ in.	Round $\frac{1}{4}$ in. dia.	Round $\frac{3}{4}$ in. dia.		
DIE CASTINGS													
X-6 .....	61.18	1.05	0.29	0.06	37.42	55,050	57,750	47,420	8.0	10.5	9.6	15+	
X-7. ....	61.10	1.01	0.80	0.03	37.06	56,020	56,450	50,480	6.0	10.4	11.9	15+	
X-9.....	60.68	1.08	1.75	0.01	36.28	53,320	56,480	45,400	5.5	8.8	8.6	13.7	
X-8 .....	60.58	0.98	1.92	0.02	36.50	51,240	54,620	46,660	3.1	7.9	9.6	13.0	
			Silicon	Manganese									
Weber Alloy.....	80.74		4.63	0.12	14.51	83,600	88,930	80,470	7.0	12.0	9.3	15+	
SAND CASTINGS—A.S.T.M. SPECIFICATION REQUIREMENTS													
A.S.T.M. B60-28.	88	8	Lead	Aluminum	4			35,000				15	
A.S.T.M. B62-28.	85	5	5		5			26,000				12	
A.S.T.M. B65-28.	63.5		2.5		34			20,000				15	
			Iron										
A.S.T.M. B59-28.	87-89	0.5	2.5-4.0	7-9				65,000				20	
				Mn		Pb							
A.S.T.M. B54-27.	55-60	0.0-1.5	0.0-2.0	0.0-1.5	38-42	0.0-0.4		65,000				25	

conformed to recommended practice for sand castings. All specimens were tested as cast, without machining of the surface; gate and fins only being removed.

The ability to die-cast a heavy section of this size is in itself an interesting illustration of the capabilities of the process.

It is evident from the data that the tensile strength of the heavy section is in general appreciably lower than the strength of the smaller section. Undoubtedly this is associated with slower cooling and less

<sup>5</sup> U. S. Patent No. 1848857.

depth of chill of the castings. There is no appreciable effect of size of section on ductibility of cylindrical specimens, although the values shown by the flat section are in general lower. This probably is related to shape of test piece as well as greater area of chill for a given mass. It should be pointed out that the flat test bar was finally abandoned by the A.S.T.M. Committee on Die Castings as not sufficiently representative, because of rather wide variation in results. Increasing lead content causes an appreciable decrease in ductility and impact resistance. Fifteen foot-pounds was the capacity of the testing machine used.

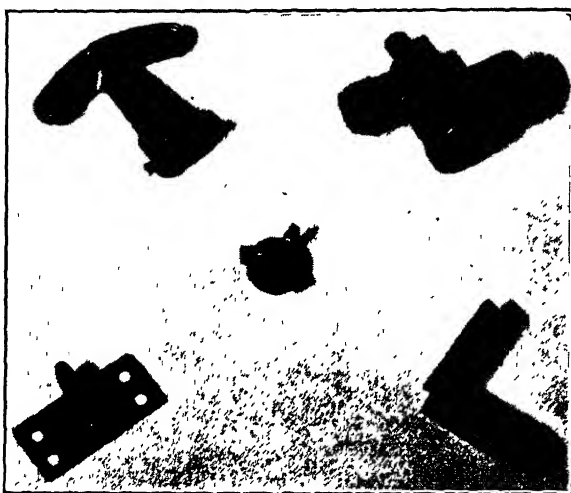


FIG. 5.—TYPES OF BRASS DIE CASTINGS.

It is of interest to compare the physical properties of brass die castings with some of the standard sand-casting alloys, some properties of which have been given in Table 1 for ease of comparison. It is evident that the die-cast alloys in general show superior tensile strength and lower elongation.

#### USE OF BRASS DIE CASTINGS

Brass die castings occupy a position between brass forgings or die pressings and sand castings. They are supplemental to die pressings, rather than competitive, although at times they may be substituted for the latter, particularly where coring will eliminate extensive machining operations. They make available complicated shapes with rather intricate coring, cast to more precise dimensions than sand castings and with a superior surface finish.

Brass die castings made in Pack and Polak machines under the relatively very high pressures available, and in dies of correct design,

are practically free from visual internal cavities but do contain microscopic blowholes and shrinkage cavities. Die castings do not have the inherent soundness of forged metal and therefore should not be used under excessive hydrostatic pressures or in parts where failure would constitute an extreme hazard.

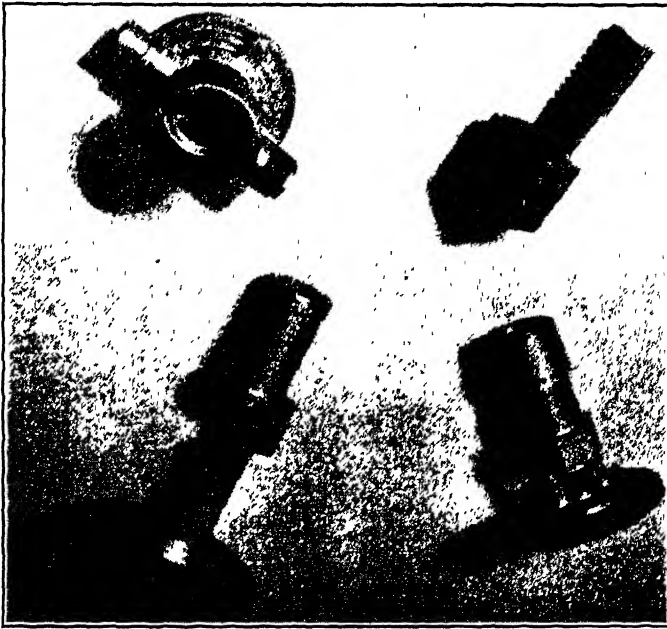


FIG. 6.—TYPES OF BRASS DIE CASTINGS.

Die-cast brass fittings have been subject to hydrostatic test pressures as high as 800 lb. per sq. in. without showing distress or leakage, which is indicative of the sound character of castings available. The actual working pressures or stresses permissible in any given case, however, depend upon design, wall section, temperature at which stress is operative and similar factors.

The parts shown in Fig. 5 and 6 illustrate several types of brass die castings that have been produced in large quantities.

## DISCUSSION

*(W. H. Finkeldey presiding)*

S. TOUR,\* New York, N. Y.—Mr. Freeman has entirely omitted to explain the basic differences between the two types of machines mentioned.

One thing to note to the Polak machine is that it is what we call a "center-gate machine," in which metal comes through one-half of the die, as distinct from the Pack

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\* Vice President, Lucius Pitkin, Inc.



machine, which is a split-gate type of machine in which the metal enters along the parting line between the two halves of the die.

The arrangement of plungers in the two types of machine should also be noted. There is no fundamental difference in the bottom plungers of the Polak and the Pack machines. The particular arrangement shown in the Polak sketch is unfortunate. It shows a pocket underneath a piston, whereas in the sketch shown for the Pack machine there is a solid plunger. The basic principles of the Polak machine permit this piston on the end of a rod to be replaced by a solid plunger, as in the Pack machine, and when this is done there is no trouble due to the metal coming down around that piston.

In the Polak machine, as this metal is forced down into the lower position the gate is opposite the middle of the slug of metal, so that the metal that is first pushed into the die is from the center of the slug and is not the scum from the top.

The base plunger principle in the Pack machine is exactly the same as in the Polak machine, but this is a split-gate type, in which the metal comes in along the parting line instead of through the cover half of the die. It is thus evident that the fundamental difference is in the type of gate and in the fact that there is one plunger instead of two.

In the Polak machine, the top plunger comes down on the metal, forces the bottom plunger to move down to a stop so as to uncover the gate hole, and then forces the metal out through the side of the slug. When the stroke is completed and the casting is made, the upward motion of the bottom plunger shears off the gate and pushes out the excess metal left in the slug. In the Pack machine, however, there is but one plunger, of which the motion is upward and which pushes the metal from the top of the slug into the gate or sprue hole.

The fundamental differences between the two machines are thus in construction and not of fluidity of the metal. There is no question that just as fluid, or just as plastic, metal can be used in one machine as in the other. The question of leakage around the bottom plunger is the same in both machines.

Mr. Freeman referred at one time to "mushy metal" and at another time to "plastic metal." In my opinion there is a difference between the two. When a metal is partially molten and partially solid we might say that it is "mushy." When it is all solidified but still quite hot it may then be in the plastic stage.

J. DIERCKX, New York, N. Y.—I do not care to criticize the remarks of the last speaker, but I happen to represent Mr. Polak, of Prague. Whether one machine is superior to the other, I do not care to discuss. I can say this, that Mr. Polak has produced his machines in Europe for a good many years and there are close to 300 of them in constant operation in all parts of Europe and working very satisfactorily. Furthermore, Mr. Polak has brought out two new types of machines working on different principles, about which more will be said at another time. If these machines had all the inherent faults mentioned, and all the drawbacks, I do not believe there would be so many of them in operation and so many being purchased.

C. PACK,\* Toledo, Ohio.—Mr. Tour has made some definite statements pertaining to the operation of the Pack and the Polak machines, which are at variance with my experience. I do not know the extent of Mr. Tour's experience with either machine, but Mr. Freeman's paper is based on some years of actual experience with both machines in the plant of the American Brass Company.

I first called attention to the successful operation of the Polak machine in 1930 in a paper read before a joint meeting of the S.A.E. and the A.S.T.M. held in Detroit.

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\* Manager, Doehler Die Casting Co.

The late Mr. W. H. Bassett was thoroughly familiar with the principles of the Polak machine at the time he decided to build the machine described in Mr. Freeman's paper as the Pack machine.

Mr. Tour properly points out that the undercut pocket formed by the underside of the plunger *P* and the cup *C* (Fig. 1, top view) is objectionable, since metal may be forced past the plunger *P* and lodge behind it. I agree with Mr. Tour that this recess is objectionable. Mr. Tour points out that no such objectionable undercut is shown by Mr. Freeman in his illustration of the Pack principle (Fig. 2). Here, again, I agree with Mr. Tour.

Mr. Tour further states that the objectionable pocket shown in the Polak illustration is not fair to the Polak machine, since this pocket is not an essential feature of the Polak principle but purely a "draftsman's accident." Here, I disagree with Mr. Tour. Patents on the Polak machine were issued in all commercial countries of the world and in every patent specification the machine shown by the inventor had the objectionable pocket. Patents were issued to Polak in this country in 1928 and reissued in 1930. In every illustration given in the patent specification, the objectionable pocket appears. Surely this must be more than mere accident.

Many papers have appeared in the European technical press written by Polak engineers and some have been reprinted in this country. In every illustration of the Polak machine appearing in these papers, the objectionable pocket appears. The first Polak machines introduced into this country were installed in the plant of the Titan Bronze Co., at Bellefonte, Pa. One of their engineers, W. W. Sieg, writing in *Iron Age*, shows the Polak principle, with the objectionable pockets. Mr. Freeman refers to the Sieg paper.

That this pocket is objectionable from a production standpoint cannot be denied, but it is inconceivable that the inventor as well as the user would continue to show this pocket if it were an inconsequential detail. As a matter of fact, a study of the Polak patent specifications will disclose the fact this pocket is a vital and essential part of the Polak principle.

Referring again to Mr. Freeman's illustration (Fig. 1) it will be noted that the casting plunger *P* is brought down under high pressure (10,000 to 20,000 lb. per sq. in.) and at a high velocity (25 to 50 ft. per sec.). The bottom of the cut *C* when properly supported takes up the shock of the blow caused by the casting operation. If the shoulder at the bottom of the cup *C* were eliminated, the machine would be entirely inoperative. No Polak machine has ever been built without the shoulder cup as illustrated in Mr. Freeman's sketch, and the undercut pockets that Mr. Tour finds objectionable cannot be eliminated without removing this shoulder.

Mr. Tour states that the Polak and Pack machines are very much alike, the only difference of any importance being that in the Polak machine the die is parted on a vertical plane whereas in the Pack machine the horizontal parting is used. The manner of parting line in any type of machine is subject to the designer's choice. The Polak machine can be built for a horizontal parting line and the Pack principle can be applied to a vertical parting line if so desired. The basic principles of both machines have been outlined by Mr. Freeman and in many other recent papers on this subject. The differences in these basic principles have also been clearly pointed out. Mr. Freeman has operated both machines for a number of years and is in a position to discuss this subject intelligently.

J. R. FREEMAN, JR. (written discussion).—This paper was written by request, with the intention of presenting it from the metallurgical viewpoint. In presenting such a new development, it seemed impossible to leave the question of the machine and its design out of the picture entirely. We have both types of machines and both are giving satisfactory results. There is no intention in the paper, nor do we desire

to imply anything in the paper, regarding the relative merits of the machines. Both are in operation and both are giving a very satisfactory product.

Referring to Mr. Tour's remarks regarding unfair comparison of physical properties of the sand castings and die castings, I think he misunderstood my point to a certain extent. I gave minimum values taken from the A.S.T.M. specifications. We know that those are minimum, and that in practice we get higher ones. The values given in the paper for the die-casting alloys are also minimum values. The compositions, naturally, are different. The comparative data give a picture of the relative properties of the two types of castings.

Regarding his statement on mushy and plastic metal, perhaps I stand corrected in that we should define what we mean by that. There is a difference between metal that has some liquid in it and metal that is completely solidified; that is below the solidus line. It may be desirable, in view of this new introduction into metallurgy of using mushy metal in a process, to draw our lines a little more clearly between "mushy" and "plastic" metals.

## Embrittlement of Uranium by Small Amounts of Aluminum and Iron

By H. W. HIGHRITER,\* MEMBER A.I.M.E., AND W. C. LILLIENDAHL\*

(New York Meeting, February, 1935)

THE method developed and used in this laboratory for the production of metallic uranium of such purity that it is ductile and can be cold-worked to fine wire or thin sheet by rolling has already been described<sup>1</sup>. It consists, briefly, in the electrolysis of potassium uranous fluoride ( $KUF_5$ ) in a molten bath composed of equal parts of sodium and calcium chlorides. The bath is contained in a graphite crucible, electrically heated to about  $775^\circ C.$ , the crucible serving as the anode for electrolysis. The uranium deposits in finely divided form mixed with salts upon a molybdenum cathode suspended axially in the crucible. Upon completion of the electrolysis the cathode is removed and cooled, the deposit broken and leached to remove salts. The metal powder is washed with water and dilute acetic acid and dried in vacuo to reduce oxidation. Suitable amounts are then pressed into pellets and heated in vacuo by high-frequency induction, using a thorium crucible. The uranium melts and flows away from the pellet, leaving a shell, which is largely oxide.

In general, this method produced a satisfactory metal, although at times the uranium was not ductile. The investigations recorded here were made to find the cause of this embrittlement.

It was known that the metal generally contained carbon, derived from disintegration of the graphite crucible in which electrolysis is conducted, in amounts dependent upon the thoroughness of washing the metal powder. Accordingly, analyses of several samples, both ductile and brittle, were made by combustion and absorption of  $CO_2$  in Ascarite, using air instead of oxygen to reduce the temperature and rate of oxidation. Several of these metals were made with special precautions to reduce carbon content. The results show no relationship between ductility and carbon content in the range investigated (Table 1).

Microscopic examination of ductile and brittle metals disclosed the presence in the latter of an intergranular constituent, harder than the matrix and less easily oxidizable, which was absent from the ductile material. Rough estimates of the volume of the hard constituent

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\* Research Department, Westinghouse Lamp Co., Bloomfield, N. J.

<sup>1</sup> Driggs and Lilliendahl: *Ind. & Eng. Chem.*, **22**, 516.

indicated that in some specimens it constituted about 15 per cent of the total volume.

TABLE 1.—*Effect of Carbon on Ductility of Uranium*

Sample No.	Character of Metal	Carbon Content, Per Cent
97	Ductile	0.03
99	Brittle	0.08
100	Brittle	0.02
101	Brittle	0.09
102	Ductile	0.08
106	Brittle	None

Figs. 1 and 2 illustrate the microstructure of brittle and ductile samples. The polished samples were heat-treated and the uranium

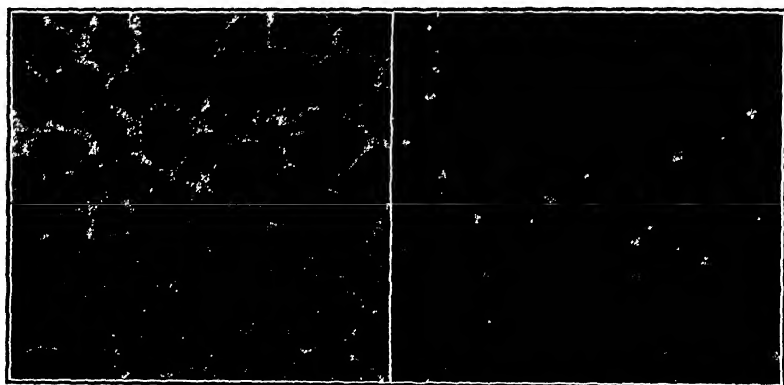


FIG. 1.—BRITTLE URANIUM, SAMPLE 104.  
× 250.

FIG. 2.—DUCTILE URANIUM, CONTAINING  
CARBIDES, SAMPLE 113. × 250.

matrix darkened by oxidation. No reagent has so far been found suitable for etching uranium free from the intergranular constituent so as to develop grain boundaries.

Both Figs. 1 and 2 show a fine cubical constituent, held to be uranium carbide  $U_2C_3$  or  $UC_2$ . Fig. 3 shows such a carbide particle forming around a graphite nucleus.

On the assumption that the intergranular constituent resulted from a metallic or nonmetallic impurity, samples of ductile and brittle material were examined spectrographically at the Bureau of Standards, with the result that the lines of iron and aluminum were found to be much stronger in the brittle sample than in the ductile metal. This was confirmed by chemical analyses of a number of samples, as indicated in Table 2.

To locate the source of the iron and aluminum, analyses were made of the "green salt,"  $KUF_6$ , and of the sodium chloride and calcium chloride that form the electrolyte. Aluminum and iron were found in small amounts in the chlorides.

An electrolysis was made, using materials containing, at the most, traces of these metals, but the resulting uranium was brittle and contained both iron and aluminum. The analysis is given in Table 2 (sample 107).

This result seemed to leave the graphite crucible as the only other possible source, which was also probable, as the crucible is the anode during electrolysis and the fused bath would have a strong solvent action on any iron and aluminum oxides present in the graphite.

These crucibles are machined from Acheson graphite electrodes, supplied by the National Carbon Co. They are available in two grades, AGR and AGX, the latter being the denser. Since crucibles of grade AGR had been used, a crucible was machined from grade AGX carbon and electrolyses made with salts containing not over 0.015 per cent iron and aluminum weighed as oxides. The resulting metal, sample 109, was ductile and low in Fe and Al (Table 2).

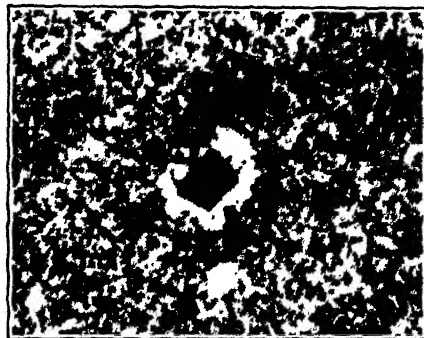


FIG. 3.—URANIUM CARBIDE FORMED AROUND GRAPHITE NUCLEUS.  $\times 2000$ .

TABLE 2.—*Chemical Analyses*

Sample No.	Character of Metal	Iron, Per Cent	Aluminum, Per Cent
98	Ductile	Trace	Trace
104	Brittle	0.27	0.23
107	Brittle	0.35	0.13
109	Ductile	0.03	0.03

Analyses of these two grades of carbon for iron and aluminum disclosed the following: AGX carbon contained 0.02 per cent Fe and no Al; AGR carbon contained 0.12 per cent Fe and 0.07 Al. These analyses confirm the AGR graphite used in this work as the source of iron and aluminum. It is not known that this difference between the two grades is consistent.

To investigate the effect upon uranium of these elements singly and together alloys were prepared by addition to ductile metal 109. The

mixed metal powders were pressed and treated to fusion in vacuo, in the usual manner for uranium, and the alloys analyzed, examined microscopically and cold-rolled. The results obtained are given in Table 3, which shows that 0.2 per cent aluminum produced serious embrittlement, while 0.53 per cent iron did not, although the latter increased hardness slightly more than did the aluminum.

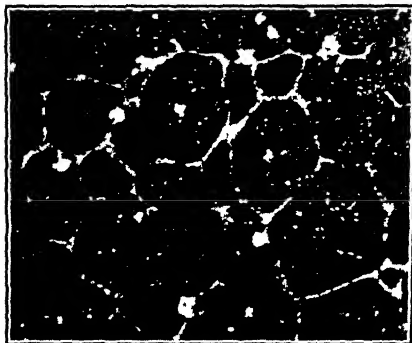


FIG. 4.—DUCTILE URANIUM CONTAINING 0.53 PER CENT FE, SAMPLE 115.  $\times 250$ .

These alloys of uranium with iron and/or aluminum show the presence of intergranular constituents, as may be seen from Figs. 4, 5 and 6. While these constituents have not been definitely

identified, it is believed, from observations of a later series of alloys, that iron forms no solid solution in uranium, but is rejected as a eutectic

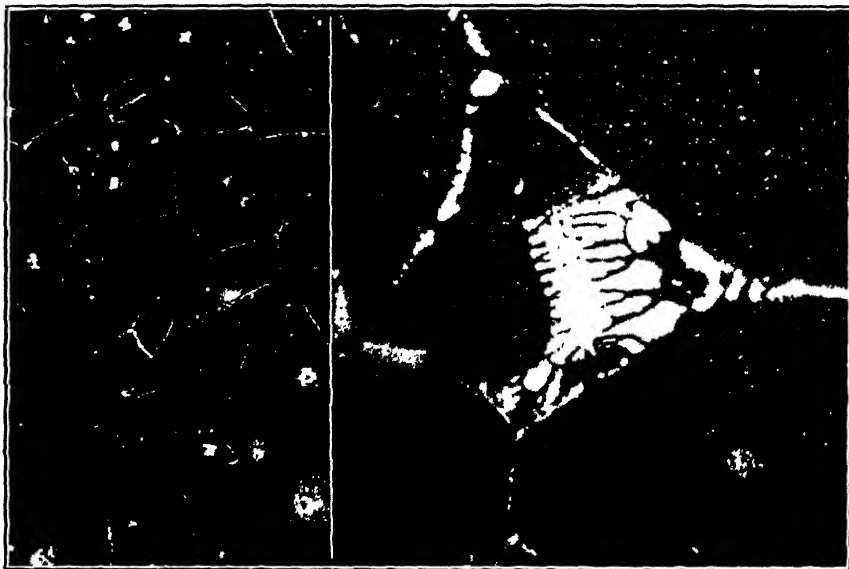


FIG. 5.

FIG. 6.

FIG. 5.—BRITTLE URANIUM CONTAINING 0.38 PER CENT FE AND 0.32 PER CENT AL, SAMPLE 114.  $\times 250$ .

FIG. 6.—INTERGRANULAR CONSTITUENT IN BRITTLE URANIUM, CONTAINING 0.38 PER CENT FE AND 0.32 PER CENT AL, SAMPLE 114.  $\times 1500$ .

containing approximately 5 per cent of iron. Polushkin<sup>2</sup> has found the compound  $\text{Fe}_5\text{U}$  in alloys low in carbon and high in uranium. It may be

<sup>2</sup> Polushkin: *Carnegie Schol. Mem.*, Iron and Steel Inst., 10, 129-50.

this compound that forms the eutectic with uranium. Fig. 4 is typical of the constituent caused by iron.

TABLE 3.—*Effect of Aluminum and Iron on Uranium*

Sample No.	Additions Made, Per Cent	Analysis, Per Cent		Character of Metal	Rockwell Hardness
		Fe	Al		
113	None	0.04	0.01	Ductile	B95
112	0.40 Al	0.07	0.20	Brittle	B100
115	0.50 Fe	0.53	0.10	Mod. ductile	B102
114	0.50 Al	0.38	0.32	Brittle	B103
	0.30 Fe				

Increasing amounts of aluminum cause the separation of an intergranular constituent which differs in appearance from that due to iron. It is illustrated in Fig. 5, at higher magnification, in Fig. 6. It is believed to be a uranium aluminide.

### CONCLUSIONS

It has been found that electrolytic uranium is embrittled by about 0.20 per cent aluminum, or about 0.5 per cent iron, or by smaller amounts when in combination. Small amounts of carbide have been found to be without adverse effect upon ductility.

The source of these impurities has been found to be the graphite crucible used for electrolysis, although contamination by the use of impure sodium and calcium chlorides for the electrolyte would be equally deleterious.

### DISCUSSION

(*Wheeler P. Davey presiding*)

E. P. POLUSHKIN,\* New York, N. Y. (written discussion).—In connection with the nature of intergranular constituent described by the authors, it is interesting to compare Figs. 1 and 5. These figures represent two specimens, Nos. 104 and 114, of brittle uranium. The amount of intergranular constituent in the first figure is considerably larger than in the second. Comparing chemical composition of these specimens, we find that the second (No. 114) has a greater proportion of iron and aluminum, the average difference for both elements being about 0.1 per cent. If the occurrence of intergranular constituent is attributed to the presence of iron and aluminum in uranium, how to explain that with the increase of these elements, the proportion of intergranular constituent is markedly lowered? Assuming that in specimen No. 114 iron and aluminum were partly retained by uranium, we must conclude that these elements can form a solid solution with uranium. Then it is probable that by a certain heat-treatment the intergranular constituent can be entirely eliminated.

\* Metallurgical Engineer, Lucius Pitkin, Inc.



H. W. HIGHWRITER AND W. C. LILLIENDAHL (written discussion).—Dr. Polushkin has raised a question that has given us some concern, although our interpretation of the differences to which he calls attention is different from his.

The samples of uranium discussed in the paper are quite small and probably not homogeneous. The distribution of iron and aluminum appears to vary somewhat throughout the fused buttons and makes difficult a correlation between the amount of constituents in the microstructure and the chemical composition.

Sample 114, which shows a smaller amount of intergranular constituent than sample 104, although higher iron and aluminum contents, was prepared by the addition of iron and aluminum to the uranium before fusing. It is possible that in the time allowed there was not complete conversion of the iron and aluminum to the form in which they appear in the intergranular constituent, therefore the amount of the latter would be less than indicated by the analysis.

## Welded Pressure Vessels

BY R. K. HOPKINS,\* MEMBER A.I.M.E.

(New York Meeting February, 1935)

For a great many years fusion welding has been used in and around petroleum refineries, but it is only within six or seven years that the more important pressure vessels have been constructed by this process, because before that time the properties of fusion welds would not withstand such rigorous service. Since the adoption of fusion welding for the construction of this equipment, the refiner has required pressure vessels suitable for operation over a very wide range of conditions. On the one hand, vessels must operate at extremely high temperatures, in the range of 950° to 1000° F., and on the other vessels must be suitable for operation at sub-zero temperatures down as low as -75° F. Also, vessels are required suitable for operation at pressures upwards of 1000 lb. per sq. in., and as low as a 29-in. vacuum. In addition, vessels are required to withstand the attack of very corrosive mediums. It has been a rather difficult task for the fabricator to meet all of these requirements, but as a result of the extensive research carried on by steel manufacturers and several fabricators of class I vessels, practically all of these demands have been met.

In order to meet the refiners' requirements for this wide range of conditions, the fabricator has worked closely with the metallurgist. This has enabled him to choose the proper base metal for each service condition, but it has been the fabricator's problem to develop a welding rod and welding technique, as well as a heat-treatment, that would produce in the welded vessel characteristics in and around the weld comparable to those in the base metal.

Where corrosion is not a serious problem, and where the operating temperatures are not too high, ordinary carbon steel has served very well. But when corrosion is serious, and/or when the temperatures are either very high or very low, it is necessary to use some form of alloy steel to give satisfactory service.

A great deal of credit is due to the members of the Boiler Code Committee and also to the members of the Joint A.P.I.-A.S.M.E. Committee, who have formulated codes that insure the safety of the

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Manuscript received at the office of the Institute, Feb. 21, 1935.

\* Director of Metallurgical Research, M. W. Kellogg Company, Jersey City, N. J.

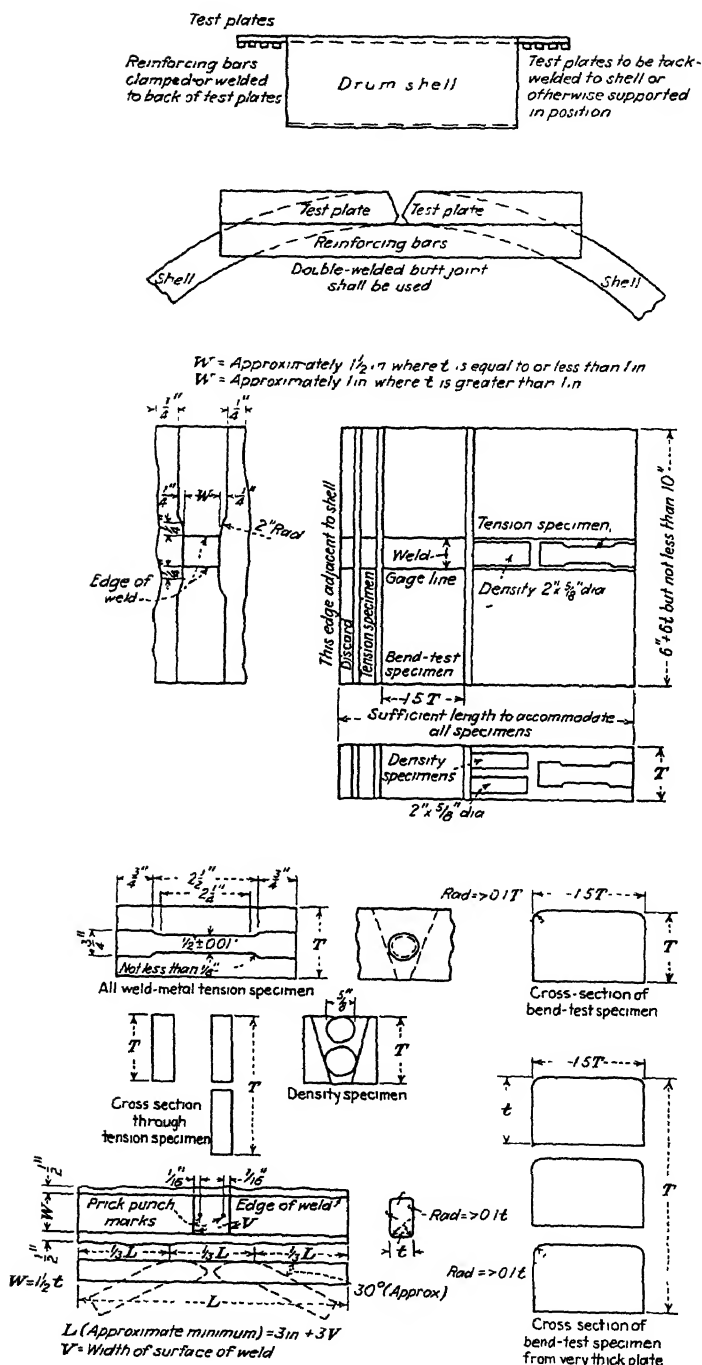


FIG. 1.—BOILER CODE REQUIREMENTS FOR CLASS I TEST PIECES.

vessels built under them by requiring that certain physical and non-destructive tests be met.

Fig. 1 gives a general idea of the physical tests required by the Boiler Code for class I pressure vessels, which are practically the same as those required by the A.P.I. code. The code requires that test plates be made of steel of the same analysis and thickness as the plates being welded. *U-9* at the top shows how these plates are attached to the end of the shell before welding. The seam in the test plates is welded as a continuation of the seam in the shell itself. By following this procedure, one is assured that the technique used on the test plates is identical to that used

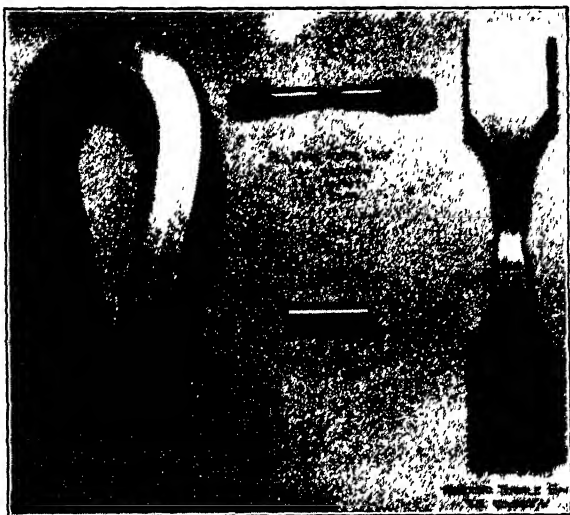


FIG. 2.—TYPICAL BROKEN BOILER CODE TEST BARS WITH AVERAGE RESULTS FOR CLASS I PRESSURE VESSELS.

on the vessel. *U-10* and *U-11*, at the bottom, show how the test plates are laid out, and the test specimens machined. The Boiler Code requires that one 0.505-in. tensile bar and a density bar be taken from the weld itself. The tensile strength of the 0.505-in. bar must at least equal the minimum tensile strength required for the plate. The elongation in 2 in. must be at least 20 per cent. The density bar must show a minimum specific gravity of 7.80. In addition to these tests, the code also requires that a reduced tensile bar and a bend bar be taken transverse to the direction of the weld. The reduced tensile bar is machined in such a way that the load is concentrated at the welded joint, thereby not only testing the strength of the weld metal itself but the fusion zone and adjacent area in the plate.

The requirement is that the tensile strength of this bar be at least equal to the minimum required for the plate. The bend bar is bent as a

free bend, and the code requires a minimum elongation of 30 per cent on the outer fibers of the weld.

Fig. 2 shows how these specimens look after test. The values given under each of the specimens represent the average of many thousands of tests. Attention is called to the extreme ductility of the weld metal, and also to the high ratio yield point to tensile strength. This is char-

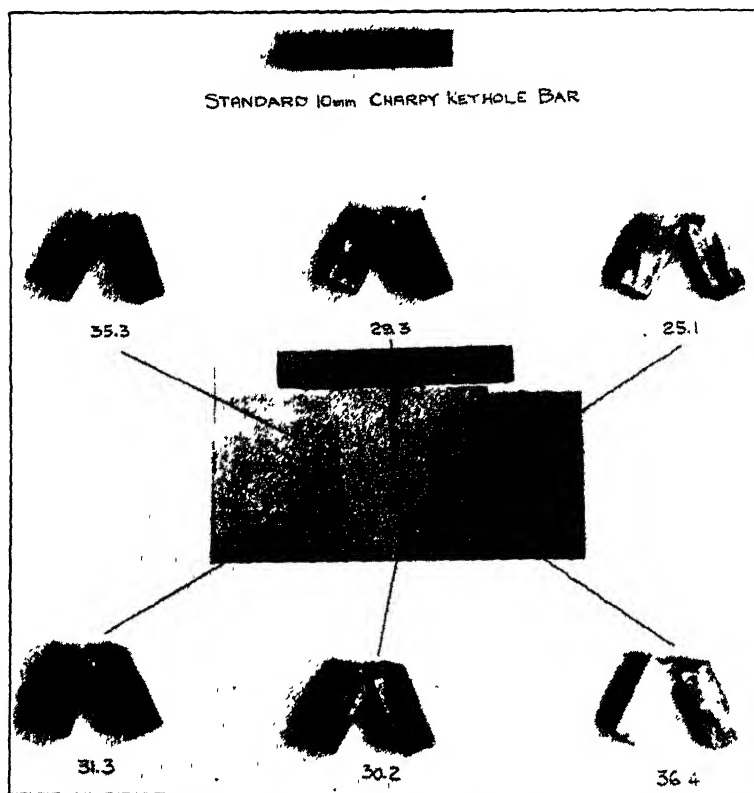


FIG. 3.—CHARPY IMPACT VALUES OF CLASS I CARBON-STEEL WELD, ADJACENT AREAS AND PLATE.

acteristic of weld metal as produced by the covered electrode with the proper welding technique.

Although neither the Boiler Code nor the A.P.I. Code requires an impact test of either weld metal or plate material, Fig. 3 is included to give an idea of the impact resistance of the weld metal and the welded joint as compared with that of the plate. These tests were run on a carbon-steel welded plate at room temperature. The values listed below each bar represent the average of three tests. The Charpy keyhole-notch type of bar was used. The impact resistance of the weld metal

taken in various sections of the weld is fairly high. That of the fusion zone is practically the same, while that of the heat-affected area of the plate and the transition zone between the heat-affected area and the base metal is still higher. The reason for this is the grain refinement in this area, which is a result of the welding process. The impact value

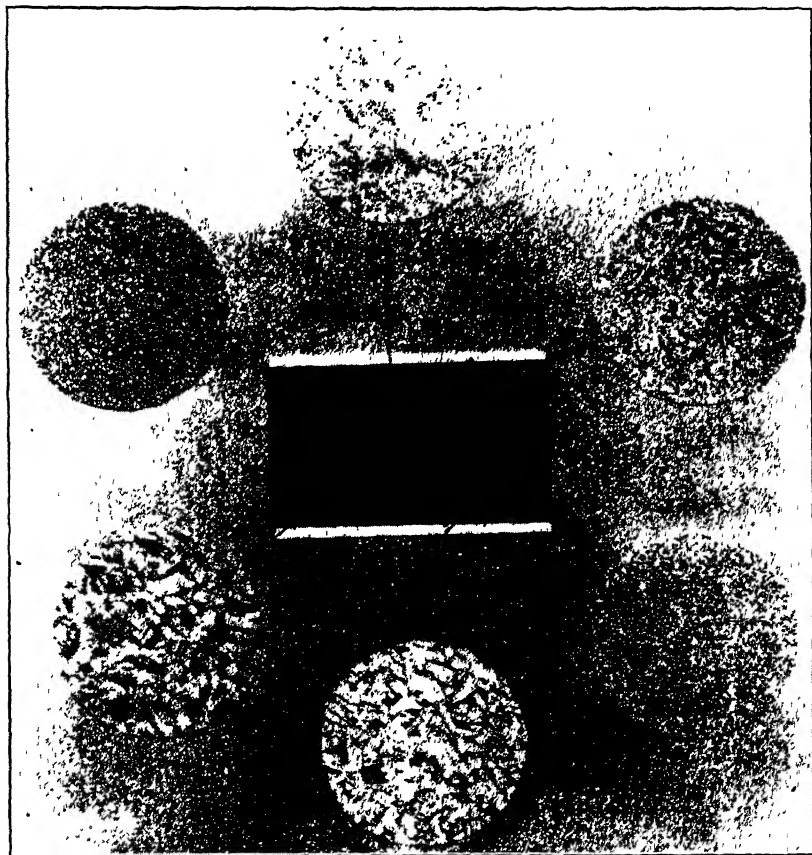


FIG. 4.—TYPICAL MICROSTRUCTURES OF CLASS I WELD AND ADJACENT AREAS.  $\times 100$ ,  
REDUCED  $\frac{3}{8}$  IN REPRODUCTION.  
Etched in 4 per cent alcoholic nitric acid.

of the plate material happens, in this particular instance, to be lower than any of the others, but this is not always true.

It is evident from Fig. 3 that the impact value of the weld metal and welded joint is satisfactory for ordinary service, and for this reason the Boiler Code does not require such a test. The Code Committee did not overlook the possible necessity for such a test, because when the code was first formulated the impact test was specified. It was only after a

thorough investigation had been made that the Code Committee deleted the requirement for this test from the code.

Fig. 4 is related in some degree to Fig. 3, inasmuch as the microstructures of the areas from which the impact bars were taken are shown. The structure of the base metal itself, although normal for this type of material, has by far the largest grain size of all. The photomicrograph in the lower left-hand corner is interesting because it shows the pearlite just beginning to break up at the edge of the transformation zone between the heat-affected area and the base metal. The grain size of the heat-affected area and of the weld is approximately the same. As shown in Fig. 3, the impact value of weld metal and adjacent area was higher than that of the plate, and the fact has been established by this, and many other tests, that the impact value is increased as the grain size is decreased.

For vessels required to operate at sub-zero temperatures, it was found that ordinary carbon steel was not suitable, because of its erratic and generally low impact resistance at the temperatures in question; namely,  $-50^{\circ}$  to  $-75^{\circ}$  F. A considerable amount of work has been done on this subject in the past two or three years, which indicates that some form of alloy steel should be used for low-temperature service where impact is a factor. Because of the relatively simple fabricating characteristics of 2.25 per cent nickel steel, and also because of its high impact values at low temperatures, this analysis has been adopted for low-temperature service by several refiners and fabricators. Unfortunately, this particular analysis is rather expensive, as compared with carbon steel, and for that reason experimental work is being carried on continually with the hope that some method will be found to insure uniformly good impact resistance at sub-zero temperatures in carbon steel, or at least in a less expensive alloy steel. It is believed that an effective control over the deoxidation practice used in making the steel will be helpful in this regard. C. H. Herty, Jr. has done some very interesting work along this line.

Fig. 5 shows the microstructure of silicon-killed low-carbon steel plate, as well as that of the adjacent area of the plate and the weld metal. The figures below the photomicrographs represent the impact value of each at  $-50^{\circ}$  F. The impact value of the plate material, as shown in the right-hand column, is extremely low, while that of the adjacent area, shown in the center column, is very good. The improvement in impact resistance is due primarily to the reduction in grain size in this area. On first glance, it would seem apparent that carbon steel would be suitable for low-temperature service if heat-treated to the proper grain size. This probably is true, but, unfortunately, it does not seem to be a practical procedure. In order to obtain a fine enough grain to insure good low-temperature impact resistance, it is necessary to drastically quench ordinary carbon-steel materials. The adjacent area in Fig. 5

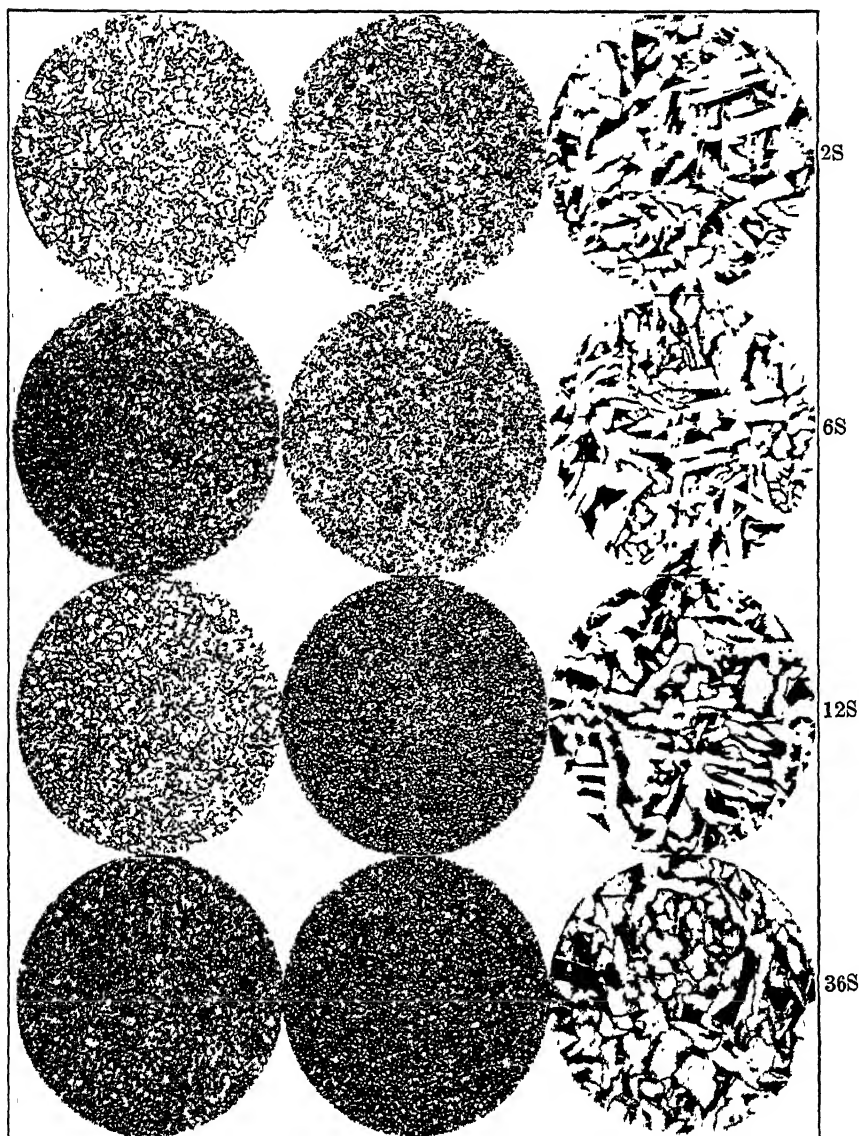


FIG. 5.—MICROSTRUCTURE OF SILICON-KILLED LOW-CARBON STEEL PLATE, ADJACENT AREA AND WELD METAL.

Left column, weld metal; center, adjacent area; right column, plate.  
Read left to right, as follows, impact values at  $-50^{\circ}\text{F.}$ :

Line 2S: 26.2, 35.5, 3.0  
Line 6S: 23.4, 25.8, 1.8  
Line 12S: 25.0, 31.9, 1.5  
Line 36S: 15.5, 26.7, 2.6



represents the structure obtained by such a quench. It is not practical to quench full thickness and full-sized carbon-steel plates to such a small grain size. The grain size at which the impact value of carbon steel falls off seems to be very critical. Some tests have been run to determine just how small the grain size should be, but with grain sizes that seemed practically identical on two samples, one would show a high impact value and the other an extremely low one. Although the impact values shown for the weld metal seem to be quite acceptable, it has been determined that such values cannot be depended upon in plain carbon steel at low

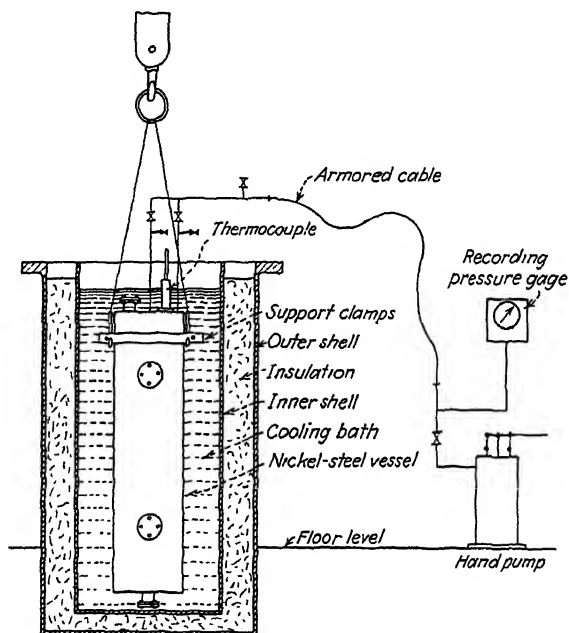


FIG. 6.—SET-UP FOR SUB-ZERO TEST ON NICKEL-STEEL TANKS.

temperatures. It is recommended, therefore, that some form of alloy-steel weld be used for this type of service.

Although 2.25 per cent nickel steel has very good fabricating characteristics and good low-temperature impact resistance, it has been shown that even this steel may, by mistreatment, be put into an unsafe condition. Table 1 gives impact values at  $+70^{\circ}$  and  $-75^{\circ}$  F. of 2.25 per cent nickel-steel plate in three heat-treated conditions. The first set of figures represents the values obtained after a stress relief at  $1150^{\circ}$  F., all of which are quite acceptable. The next set of figures, however, represents the resistance of this same material after heating for one hour at  $1900^{\circ}$  F., air cooling, reheating to  $1150^{\circ}$  F. for one hour and furnace cooling. The impact values at  $+70^{\circ}$  F. are actually higher than those shown in the first column, whereas the impact value at  $-75^{\circ}$  F.

is extremely low. The last set of figures represents the impact value of this material after heating to 1900° F. for one hour, air cooling, normalizing from 1525° F. and finally stress-relieving at 1150° F. This treatment has not only restored but actually raised the low-temperature impact resistance. The importance of these data can be appreciated when it is realized that in spinning and flanging a head for a pressure vessel the temperature to which the disk is heated for this operation is usually about 1950° F. It is evident, therefore, that unless a normalizing treatment is specified for such heads they would be unsafe for service.

TABLE 1.—*Effect of Heat-treatment on Impact Value of 2.25 Per Cent Nickel Steel*  
C, 0.24, Mn, 0.68, Ni, 2.51

Symbol	Heat Treatment				Charpy Impact, Ft.-lb. Absorbed <sup>a</sup>	
	Normalize		Draw		Temperature, Deg. F.	
	Deg. F.	Hr.	Deg. F.	Hr.	+70	-75
SCD			1150	1	37.9	20.5
SHD			1150	1	33.7	24.5
BCD			1150	1	32.3	24.2
BHD			1150	1	35.2	22.4
TCD			1150	1	31.3	18.4
THD			1150	1	36.9	21.5
SC9D	1900	1	1150	1	41.3	7.0
SH9D	1900	1	1150	1	30.7	5.1
BC9D	1900	1	1150	1	33.2	4.4
BH9D	1900	1	1150	1	30.9	3.3
TC9D	1900	1	1150	1	29.7	2.9
TH9D	1900	1	1150	1	41.8	3.5
SC9ND	1900	1	1150	1	38.5	27.9
	1525	1				
SH9ND	1525	1	1150	1	34.7	23.2
BC9ND	1525	1	1150	1	41.8	25.3
BH9ND	1525	1	1150	1	43.5	24.3
TC9ND	1525	1	1150	1	40.3	27.9
TH9ND	1525	1	1150	1	37.7	21.9

<sup>a</sup> Each figure represents average of three bars.

Although all of the laboratory data indicated that nickel steel, when properly welded, would be satisfactory for service at -50° F., additional tests were run on full-sized nickel-steel vessels. Fig. 6 shows the equipment used for cooling these vessels. Each vessel was submerged in a tank of gasoline, which itself was insulated from the atmosphere as shown.

The vessel itself was filled with gasoline and a pressure of 250 lb. was held on it with the hand pump shown at the right. A thermowell was placed in the top of the vessel, so that the temperature of the gasoline within could be noted at all times. Carbon dioxide ice was added to the gasoline surrounding the vessel until the temperature was brought down to  $-50^{\circ}\text{F}$ . This temperature was then maintained, as well as the 250-lb. pressure, for a period of 12 hr. At the end of that period, the vessel was removed quickly from the bath, lowered to within a few inches of the ground, and struck with a hammer, the full pressure being held throughout the test. The weld was hammered along its center as well as on both sides. The entire shell of the vessel, as well as the heads, was also ham-

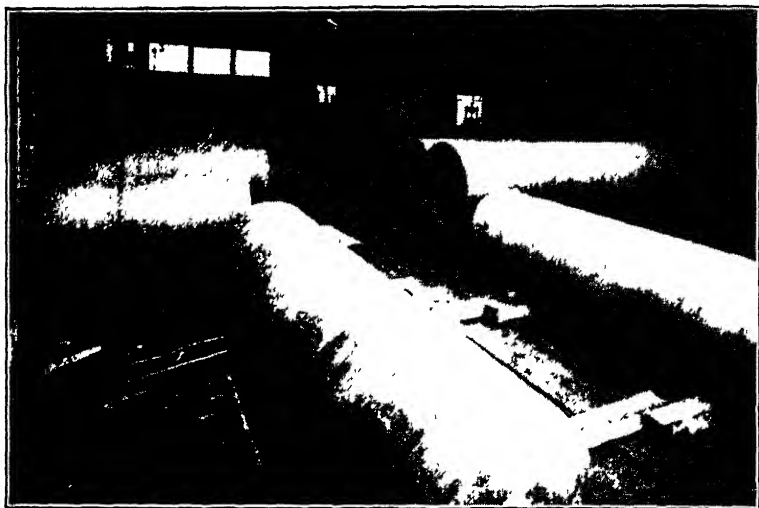


FIG. 7.—NICKEL-STEEL VESSELS IN COURSE OF FABRICATION.

mered. Several vessels were tested in this manner and no trouble was experienced. No temperature drop could be noticed in the gasoline inside the vessel during the hammer test. These vessels were put into service, and are still operating successfully.

As a result of all these tests, large nickel-steel vessels are being used in oil-dewaxing service today. Fig. 7 gives a general view of several nickel-steel vessels in the course of fabrication. The long one at the right is 11 ft. 0 in. in diameter and approximately  $1\frac{1}{4}$  in. thick.

Fig. 8 was prepared to show the types of defects that may occur in pressure-vessel welds, as well as the type of weld procurable today when proper weld rod and welding technique are used. The value of X-ray examination can be appreciated from an inspection of these three films. The cross cracks shown in the film at the left, as well as the porosity and unfused areas shown in the film at the right, cannot usually be detected by surface inspection, which shows the necessity for and value of X-ray

examination. When such defects are discovered, they may all be repaired in such a way that in a second X-ray the seam will show the same high quality as that represented by the film in the center.

The heat-treatment given welded pressure vessels before shipment, as applied to plain carbon steels and to the lower alloy steels, consists

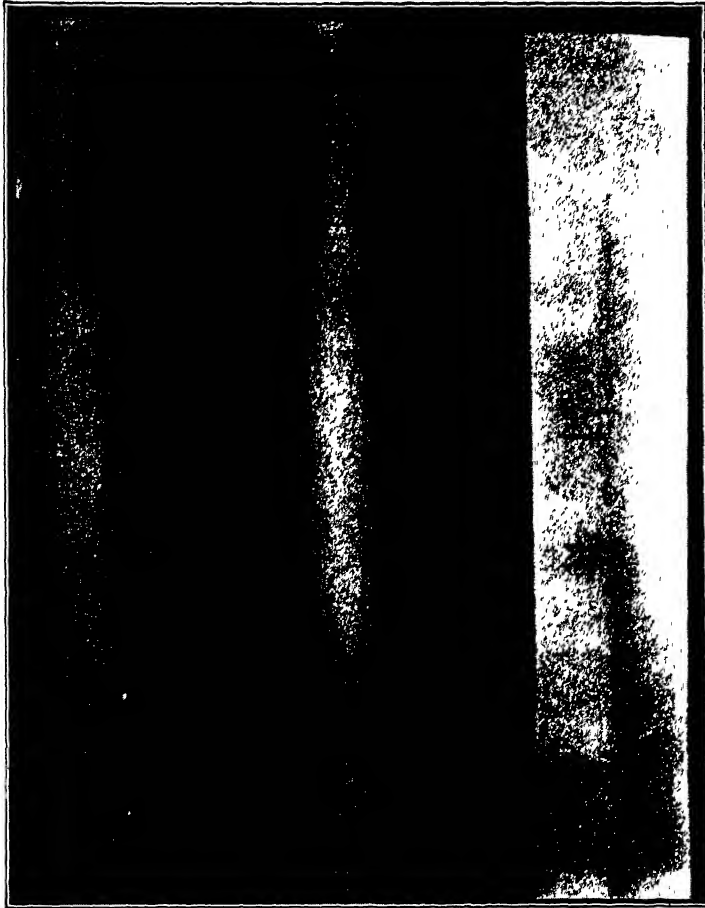


FIG. 8.—FILMS SHOWING DEFECTS IN PRESSURE-VESSEL WELDS.

primarily of a stress relief carried on at 1150° F. The temperature is held for one hour per inch of thickness and the vessel is then furnace-cooled. This treatment is looked upon usually as a means for removing strains produced by welding only, but when it is realized that vessels such as the one shown in Fig. 9 are required by the refiner today, it can be appreciated that a great many strains other than those caused by welding are set up throughout the vessel as a result of fabrication. In

such cases the stress-relieving treatment is just as important for the removal of fabricating strains as it is for the removal of welding strains.

Fig. 10 shows a reaction chamber constructed from seamless rolled sections fusion-welded together. The wall thickness of this vessel is  $4\frac{5}{8}$  in., but there is practically no limit to the thickness to which fusion-

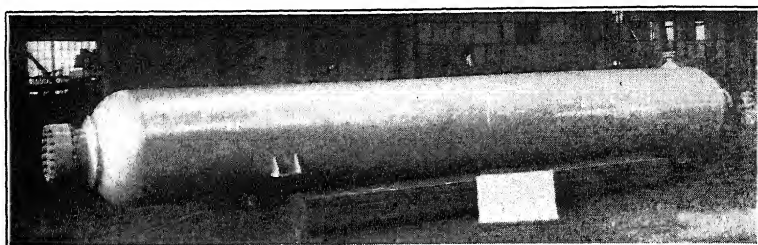


FIG. 9.—A NICKEL-STEEL PRESSURE VESSEL.

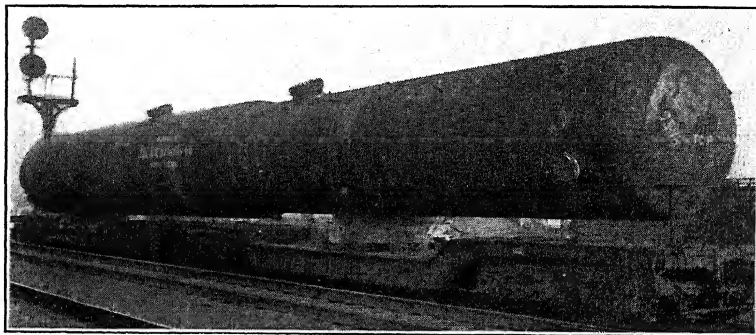


FIG. 10.—REACTION CHAMBER CONSTRUCTED FROM SEAMLESS ROLLED SECTIONS FUSION-WELDED TOGETHER.

welded vessels can be furnished. Vessels fabricated from such sections are given the same heat-treatment as those fabricated from plate.

Although the fabrication and heat-treatment of high-alloy steels for corrosion resistance and extremely high-temperature service is more difficult than for carbon-steel construction, the class I fabricator today is in a position to furnish the refiner with pressure vessels for practically any type of service.

# Some Mechanical and Metallurgical Aspects of Present-day Oil-production Equipment

BY ALBERT G. ZIMA\*

(New York Meeting, February, 1935)

ACCORDING to recently published statistics, it is predicted that as much oil must be produced during the next 16 years as has been produced during the past 75, in order to satisfy the high rate of consumption of petroleum products. During 1934, over 17,000 oil wells were completed in the United States, and it is expected that over 20,000 additional wells will be drilled during the current year.

Were it not for the remarkable progress made during recent years in the improvement of drilling technique and in the development of equipment used in the production phase of the oil industry, it is doubtful whether sufficient oil could be produced to meet present requirements. A few years ago, wells seldom were deeper than 3500 to 4000 ft., owing to the limitations of the drilling methods and equipment employed. Today, however, through the application of scientific drilling methods and the adaptation of modern equipment and improved materials, many wells range from 6000 to 8000 ft. in depth, and a few recent completions exceed 10,000 feet.

## DRILL TOOLS

Modern rotary drilling tools are the product of ingenious design and careful selection and adaptation of materials used in their construction. They must withstand terrific abrasion and, because of their compactness, must be designed to resist exceedingly high unit stresses. In bits, core drills and reamers, the bodies are made of either forged or cast alloy steels, heat-treated to develop a combination of high strength and toughness. To provide sufficient strength to the threaded portions and to protect the threads from distortion or damage, the box or pin sections of the tools are hardened to approximately 310 to 330 Brinell hardness number. Drill and reamer cutters are generally of the movable type; i.e., serrated cones, cylinders or disks, which can readily be replaced when

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\* Development and Research Dept., International Nickel Co., New York, N. Y.

TABLE 1.—Some Alloy Steels Used in Various Parts of Oil-production Equipment

Part	Mechanical Requirements	Steel	Typical Mechanical Properties					
			Yield Point Lbs./Sq. In.	Tensile Strength Lbs./Sq. In.	Elong. in 2% (%)	Red. of Area (%)	Brinell Hard- ness	Isod Impact Ft. Lbs.
Rock drill and reamer cutters, fishing taps, slip inserts. Reamer and drill cutter pins are sometimes made of these steels.	High surface hardness for wear resistance, tough shock-resisting core.	S. A. E. 3115, carburized: 1475° F., oil quench 1550° F., oil quench 1400° F., oil quench }	125,000	155,000	13	43	335	30
			85,000	125,000	25	55	255	55
		S. A. E. 4615, carburized: 1625° F., oil quench 1550° F., oil quench 1425° F., oil quench }	105,000	145,000	17	52	300	35
			75,000	110,000	28	57	215	75
Rotary machine gears.		S. A. E. 2315, carburized: 1475° F., oil quench 1325° F., oil quench 1375° F., oil quench }	135,000	180,000	11	47	345	35
			90,000	95,000	35	65	195	85
		S. A. E. 2315, single quenched as described above.						
		S. A. E. 3140, oil-quenched at 1475-1525° F., and tempered at: 900° F. 1000° F.	135,000 118,000	192,000 143,000	19 17	53 57	330 283	40 55
Bodies for drills, reamers, casing perforators, miscellaneous drilling and fishing tools, tool joints, drill collars, Kellys, piston rods for slush pumps, miscellaneous shafting for draw works, etc.	High strength together with good toughness and fatigue properties in pieces of medium and heavy section.	S. A. E. 2340, oil-quenched at 1400-1450° F., tempered at: 900° F. 1000° F.	140,000 120,000	155,000 136,000	18 21	57 60	338 300	36 50
			180,000 to 225,000	200,000 to 265,000	15 to 8	45 to 33	400 to 500	25 to 8
Reamer and drill cutter pins, rotary machine gears and pinions.	High hardness with toughness.	S. A. E. 3250, 4650, 6150, oil-quenched and tempered.	125,000 to 180,000	160,000 to 210,000	17 to 10	60 to 42	300 to 400	50 to 10
		S. A. E. 4140, 3140, oil-quenched and tempered.						
Wall-scraper blades, fishtail blades.	High hardness and strength.							

worn out. Usually, these cutters are machined from low-carbon nickel-alloy steel forgings and subsequently case-hardened to impart the necessary wear resistance. The cutters are mounted by means of suitable bearings upon axles or pins and in this manner attached to the body. These pins are also made of alloy steel hardened to a high degree to provide wear resistance. Some manufacturers use oil-hardening steels for the pins while others use the low-carbon carburizing types such as those used for the cutters. In either case, it is necessary to produce a pin having high surface hardness (65 to 80 sclerescope) for wear resistance and sufficient strength and toughness to withstand the high stresses encountered in service. Fishtail bits used in soft-formation drilling are equipped with stationary cutters or blades made of forged or cast alloy steel protected with a hard surfacing material.

Typical properties of several alloy steels used in various parts making up rotary drill bit and reamer assemblies are shown in Table 1.



FIG. 1.—ROLLER-BEARING ROCK BIT.  
(Courtesy Reed Roller Bit Co.)

Figs. 1 and 2 illustrate two of the latest types of rock bits. In Fig. 1, note particularly the manner in which the cutters are mounted on roller bearings. Fig. 3 illustrates a pilot bit. In service, a rock bit of smaller diameter is attached to the lower end. Fig. 4 shows the arrangement of cutters on a core bit. At the right of the photograph is shown a specimen of a rock core removed by one of these bits.

Among the recent developments in rotary drilling tools is the collapsible bit, like that shown in Fig. 5. This type of bit is best adapted for drilling in regions where soft formations predominate. The development is important from the standpoint of time saving, as it makes possible the changing of bits without removing the drill stem from the hole. In changing bits attached in the ordinary manner, from 6 to 10 hr. and sometimes even more is required to remove the drill stem from the hole, replace the bit and complete the "round trip" before resumption of drilling. With the collapsible bit, dull blades have been renewed at



depths below 9000 ft. in less than  $1\frac{1}{2}$  hr. In service, the assembly is lowered through the drill stem, by means of a wire line, until it reaches the bit head at the bottom where the blades automatically open out to the size of the hole being drilled and lock into position. When the bit becomes dull, an overshot—a device fitted with specially shaped jaws or clamps—is lowered through the drill stem on a wire line until it engages a spearhead on the top of the bit carrier, and the whole assembly is then brought to the surface.

Fig. 6 illustrates another recent improvement in well drilling equipment; namely the core-taking fishtail bit, with which a core can be taken in soft formation while drilling a full-sized hole. It is



FIG. 2.

FIG. 2.—HUGHES THREE-CONE ROCK BIT. (Courtesy Hughes Tool Co.)



FIG. 3.

FIG. 3.—PILOT BIT. (Courtesy Hughes Tool Co.)

not necessary to remove the drill stem and bit from the hole to obtain the core, as the core barrel is brought to the surface through the drill stem by means of an overshot attached to a wire line. The “fish-tail” blades are made of alloy-steel drop forgings, hard-surfaced with tungsten carbide, heat-treated, and then welded to the alloy-steel bit body.

In all of the tools just described, compactness without impairment of strength or drilling efficiency is achieved through careful selection and heat-treatment of alloy steels.

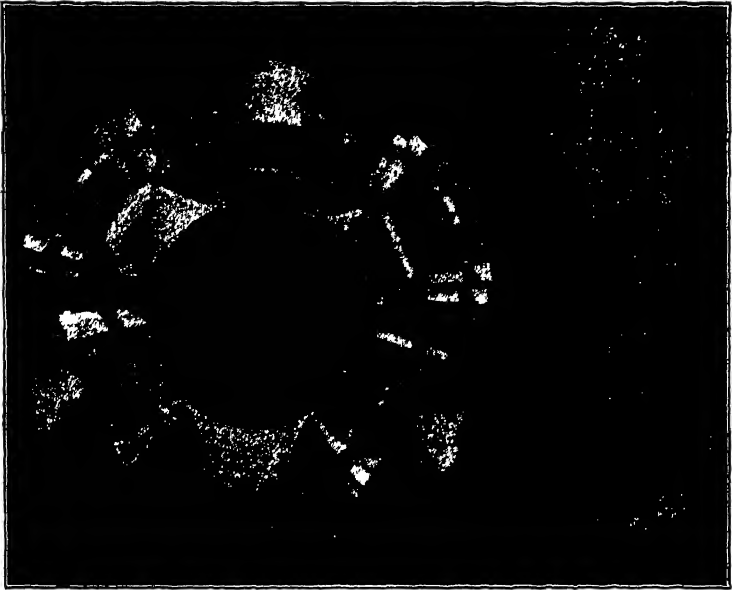


FIG. 4.—ARRANGEMENT OF CUTTERS ON HUGHES CORE BIT. (*Courtesy Hughes Tool Co.*)



FIG. 5.—“WIRE-LINE” DRILLING BIT. (*Courtesy Reed Roller Bit Co.*)

## ALLOY-STEEL KELLYS AND DRILL COLLARS

The use of long kellys has certain advantages, which are obvious to those familiar with rotary drilling practice. A considerable saving of time is effected through the use of a long kelly, since fewer interruptions of drilling for making connections to drill pipe are required than when a

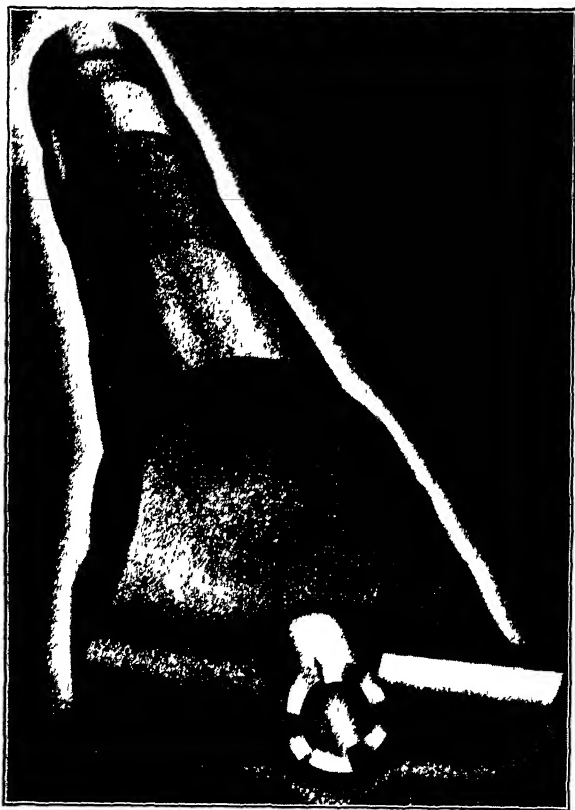


FIG. 6.—“BARRETT-ROBISHAW” CORE-TAKING BIT. (Courtesy Reed Roller Bit Co.)

short kelly is employed. Fig. 7 illustrates a 7 by 7-in. kelly 55 ft. long, recently developed by the Baash-Ross Tool Co. of Huntington Park, Calif. These pieces are forged from a medium carbon alloy steel and a 4-in. dia. hole is bored from end to end. When gaging the accuracy of the bore, a  $3\frac{13}{16}$ -in. dia. bar 6 ft. long must pass through the forging without difficulty. The ends of the stem are upset to 9-in. dia. rounds, thus providing a joint equal in strength to the square body. These ends are separately heat-treated to provide the proper degree of strength and hardness for the threads.

The 7-in. drill collars shown in Fig. 8 are also 55 ft. long and like the kellys, have a 4-in. dia. hole bored from end to end with the same degree of accuracy. Six feet of the lower end of each collar is upset to 7½-in. dia. and the threaded ends are separately heat-treated.

### TOOL JOINTS

During the early history of rotary drilling, no attempt was made to standardize dimensions or design of tool joints, and as the stresses encountered were not severe, metallurgical specifications were not considered important. As the industry progressed, however, heavier equipment was adopted and deeper wells were drilled, with an accompanying increase in tool-joint failures. The use of a plain 0.30 to 0.40 carbon steel, heat-

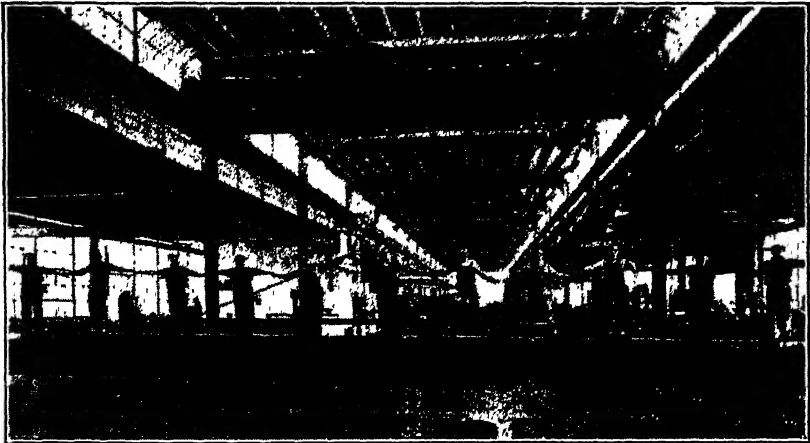


FIG. 7.—SQUARE KELLY, 55 FEET LONG, 7 BY 7 INCHES. (Courtesy Baash-Ross Tool Co.)

treated to approximately 200 Brinell, was probably the first step toward improvement. To satisfy the requirements of present drilling practice, however, alloy-steel tool joints are used almost universally. The machined forgings are oil-quenched and tempered to a Brinell hardness of 310 to 330, to provide strength and sufficient hardness of thread to prevent galling or seizing.

The availability of reliable alloy steels has contributed much to the success and practicability of the full-hole tool joint (Fig. 9). At the time the full-hole joint was first offered to the industry, it was intended primarily to accommodate the use of collapsible drilling bits like those described earlier in this paper. Although the advantages of unrestricted flow of drilling mud were noted, this feature was not fully appreciated at that time. However, as drilling speeds were increased and deeper wells were produced, the importance of increased mud circulation as a material aid to rotary drilling was recognized. Larger pumps, capable of handling

greater volumes of fluid at higher pressures were adopted and with this it soon became evident that removal of tool-joint restriction to mud flow was very desirable. Today, many thousands of full-hole tool joints, made from carefully selected alloy-steel forgings and heat-treated to insure the proper degree of hardness and the utmost in strength and toughness are in successful service.



FIG. 8.—DRILL COLLARS, 55 FEET LONG, 7 INCHES OUTSIDE DIAMETER, 4 INCHES INSIDE DIAMETER. (Courtesy Baash-Ross Tool Co.)

Typical mechanical properties of test specimens cut from heat-treated S.A.E. 3140 tool joint forgings, are as follows: yield point, 115,000 lb. per sq. in.; tensile strength, 130,000 lb. per sq. in.; elongation in 2 in., 21.0 per cent; reduction of area, 60.0 per cent; Brinell hardness, 328.

Tool-joint failures often can be traced to causes that might have been avoided through proper precautions. During a recent survey by the author, among several Texas oil producers, it was found that galling and seizing of tool joints rarely occurred where care was taken to clean the threads and lubricate them properly before making up a string. A few cases of galling were traced to improper heat-treatment of the finished pieces, resulting in slight decarburization of the surface metal. Labora-

tory tests conducted on specimens of the box and pin sections of one of the defective joints showed that by recarburization of the surface by means of a cyanide treatment and subsequently tempering to 310 to 330 Brinell, the tendency toward galling was eliminated.

Fatigue failures can be minimized through careful inspection of equipment with particular attention to exposed threads or other conditions that might result in high stress concentration. It is the author's opinion that some tool-joint failures start from the *inner* surface of the joint as the result of fatigue accelerated by high stress concentration at the root of a thread or at some point of abrupt dimensional change.

In a recent paper dealing with the effect of grooves and fillets upon highly stressed automobile and truck axle shafts, Forrest F. Johnson<sup>1</sup> described some interesting endurance tests made on several bars of S.A.E. 3140 steel, heat-treated to a hardness of 321 Brinell and "necked" in the center as shown in Fig. 10. The specimens were subjected to a surface stress of 77,000 lb. per sq. in., at their minimum diameters on a rotating-beam fatigue-testing machine of the Farmer or Wöhler type. The following "life values" were obtained before failure of the respective specimens: bar A, 81,000 revolutions; bar B, 75,400; bar C, 19,000; bar D, 14,450; bar E, 13,530; bar F, 13,800; bar G, 12,650. These data show clearly the importance of stress distribution with respect to endurance.

#### DRILL PIPE, CASING, AND OIL-WELL TUBING

Carbon and pearlitic manganese steels are used, almost entirely, for drill pipe. Although considerable study is being given to the effect of corrosion and hydrogen sulfide embrittlement upon the fatigue resistance of drill pipe, the scope of this paper will not permit a discussion of this complex subject here. It is probable, however, that the excellent results obtained with alloy-steel sucker rods in certain troublesome wells may point the way out of this difficulty.

The development of low-cost corrosion-resistant materials for casing and tubing offers a fruitful field for metallurgical research. Steels



FIG. 9.—FULL HOLE TOOL JOINT. (Courtesy Reed Roller Bit Co.)

<sup>1</sup> F. F. Johnson: Effects of Groove and Fillet Shapes on Endurance of Heat-Treated Steel. *Automotive Industries* (Sept. 22, 1934) 352-353.

possessing satisfactory mechanical and corrosion-resistant properties, are not yet available at a cost commensurate with the large tonnage requirements.

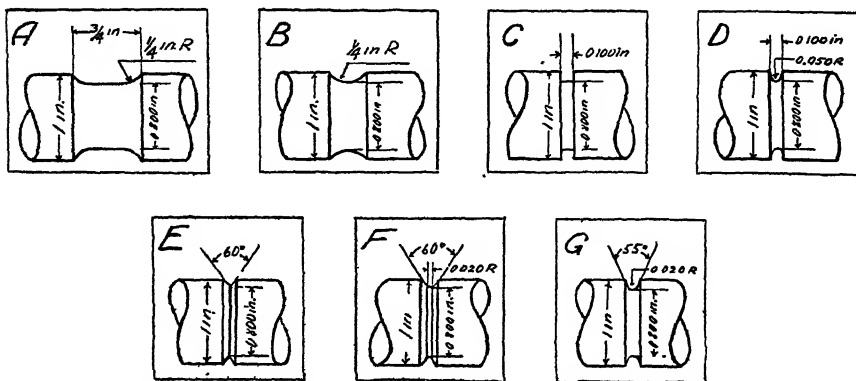


FIG. 10.—SPECIMENS USED IN ENDURANCE TESTS. (Johnson: *Automotive Ind.*)

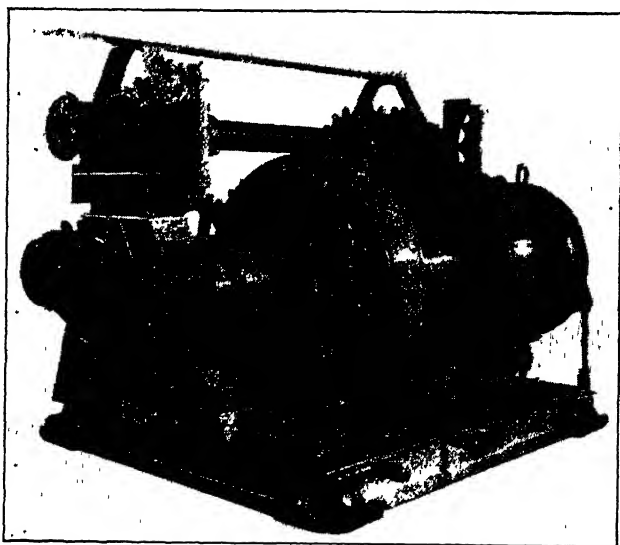


FIG. 11.—IDECO-UNITARY DRAW WORKS. (Courtesy International Derrick & Equipment Co.)

All cast parts of nickel-chromium steel, and brake bands of high-carbon nickel-molybdenum steel.

#### MISCELLANEOUS EQUIPMENT

Tremendous stresses are encountered by the gears of rotary machines, particularly in deep-well drilling. Oil-quenched and tempered alloy steels are used extensively for these parts, although some manufacturers prefer the carburized steels. Properties of some typical steels used are shown in Table 1.

TABLE 2.—*High-test Alloy Cast Iron*  
TENSILE STRENGTH, 40,000 to 48,000 LB. PER SQ. IN.

Column	1	2	3	4	5	6	7	8	9	10	11	12
Section, in. ....	$\frac{1}{4}$ to $\frac{1}{2}$ 180	$\frac{1}{4}$ to $\frac{1}{2}$ 220	$\frac{1}{4}$ to $\frac{1}{2}$ 260	$\frac{1}{2}$ to 1 180	$\frac{1}{2}$ to 1 220	$\frac{3}{8}$ to 1 260	1 to 2 180	1 to 2 220	1 to 2 260	2 to 4 180	2 to 4 220	2 to 4 260
Brinell hardness number .	Readily	Good	Economically	Readily	Good	Economically	Readily	Good	Economically	Readily	Good	Economically
Machinability . . . . .	Good	Very good	Excellent	Good	Very good	Excellent	Good	Very good	Excellent	Good	Very good	Excellent
Wear resistance . . . . .	<sup>b</sup>	<sup>c</sup>	<sup>c</sup>	<sup>b</sup>	<sup>c</sup>	<sup>c</sup>	<sup>b</sup>	<sup>c</sup>	<sup>c</sup>	<sup>b</sup>	<sup>c</sup>	<sup>a</sup>
Density . . . . .	3 20-3.40	3 10-3	3 00-3	3 10-3	3 20-3	3 28-3	3 00-3	3 00-3	3 28-3	3 00-3	3 28-3	3 00-3
Total carbon . . . . .	0 55-0 75	0 55-0 75	0 55-0 75	0 75-0 95	0 75-0 95	0 75-0 95	0 75-0 95	0 75-0 95	0 75-0 95	0 75-0 95	0 75-0 95	0 75-0 95
Manganese . . . . .	0 30	0 30	0 30	0 20	0 20	0 20	0 20	0 20	0 20	0 20	0 20	0 20
Phosphorus . . . . .	0 10	0 10	0 10	0 10	0 10	0 10	0 10	0 10	0 10	0 12	0 12	0 12
Sulfur . . . . .	1 60-1 80	1 40-1 60	1 20-1 40	1 20-1 40	1 10-1 30	1 00-1 20	1 00-1 20	1 00-1 20	1 00-1 20	1 10-1 30	1 00-1 20	1 00-1 20
Silicon . . . . .	1 25	1 25	2 00	1 25	1 75	1 75	1 25	1 75	1 75	1 25	2 00	2 00
Nickel . . . . .	None	None	None	None	None	0 25-0 35	None	None	0 25-0 35	0 25-0 35	0 35-0 45	0 50-0 60
Chromium . . . . .												

<sup>a</sup> Maximum. <sup>b</sup> Sound within section limits at top of column. <sup>c</sup> Sound throughout widely varying sections.



Another important unit of a drilling rig is the draw works. These machines must often withstand very severe static and dynamic stresses, and therefore must be strongly built. Cast alloy steels are used extensively for sprockets, gears, drum heads, spools, clutch blocks, and other miscellaneous highly stressed parts. The following mechanical properties are typical of these steels in the normalized and drawn condition: yield point, 65,000 lb. per sq. in.; tensile strength, 100,000 lb. per sq. in.; elongation in 2 in., 20.0 per cent; reduction of area, 40.0 per cent; Izod impact test, 35 ft.-lb. Fig. 11 shows a modern draw-works machine

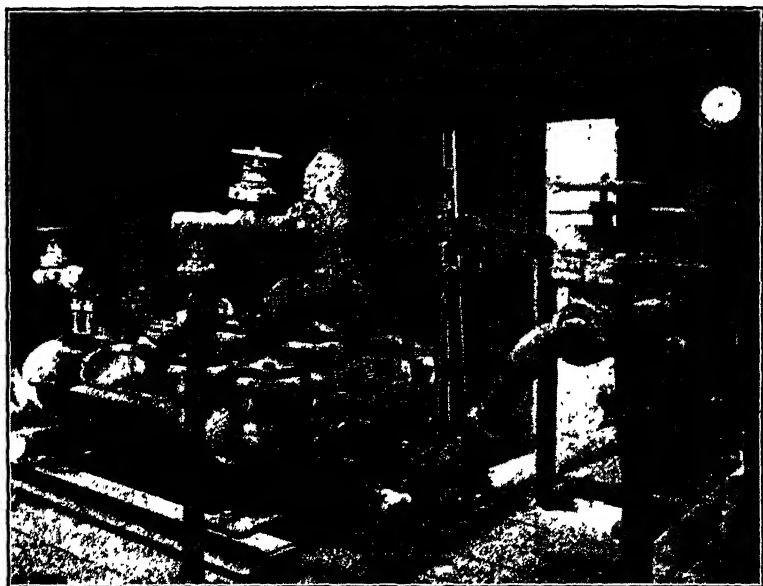


FIG. 12.—GARDNER-DENVER STEAM PUMP OPERATING IN CALIFORNIA OIL FIELD.

equipped with a newly developed nickel-molybdenum steel brake band, possessing a tensile strength of approximately 200,000 lb. per sq. in. Brake bands made from this steel retain their shape during handling, and in service behave much like a spring in clearing the brake lining from the drum when the brake is released.

Crown and traveling blocks must be strongly built to withstand the severe loads imposed upon them during drilling. They are frequently subjected to severe shock or impact loads when pulling casing or when performing a fishing operation. Alloy-steel bearings and pins are used almost exclusively in the construction of this equipment. The sheaves and spacers, which are subjected to considerable abrasion by the wire rope, are generally cast from austenitic manganese steel. A recent trend in sheave development, however, is toward the use of medium carbon low-alloy cast steels, which can be readily machined to accurate dimensions

and subsequently heat-treated to the degree of hardness best suited to the service conditions.

### ALLOY CAST IRONS

The alloy cast irons form an important group of materials used in the construction of oil-production equipment. Low-alloy cast irons are used extensively by manufacturers of pumps, compressors, valves, oil and gas engines, etc., where readily machinable castings having high tensile properties are desired. The use of heat-treated, centrifugally cast cylinder liners for slush pumps and diesel engines made of alloy cast iron is now generally recognized as an economical and convenient means of improving the performance of this type of equipment. Fig. 12 shows a slush pump equipped with alloy cast-iron pistons, cylinder liners and valve platecovers. This iron, containing from 1.25 to 1.75 nickel and 0.30 to 0.40 chromium, can be machined readily to a fine smooth finish. The tensile strength is 45,000 lb. per sq. in., or more, and the castings are of uniform density and hardness throughout their heaviest sections. Cast iron of a similar type is also used extensively for pipe-line pump construction, for liners, heads, plungers, fluid bodies and fittings. Some manufacturers are now using alloy cast iron having tensile strengths greater than 50,000 to 60,000 lb. per sq. in., for high-pressure compressors, pumps, valves and fittings. The data contained in Table 2 are representative of average results obtained in commercial foundries with cast irons of the 40,000 to 50,000 lb. per sq. in. class.

Alloy cast irons are used extensively for the working barrels and plungers of oil-well pumps. These castings are usually rough-machined and heat-treated to a hardness of 500 to 550 Brinell, and subsequently ground to a smooth finish.

Among the highly alloyed cast irons, the austenitic type, containing 14.0 nickel, 6.0 copper and 2.0 to 3.0 chromium, is finding wide application for such parts as pump and valve bodies and trim in pipe-line equipment where resistance to corrosion is important. A modification of this material possessing a tensile strength range from 60,000 to 100,000 lb. per sq. in., with elongation in 2 in. of 8 to 25 per cent, is being developed for pipe-line flanges and bolts subjected to severe corrosion.

### CONCLUSION

Modern oil-production practice offers to the engineer and metallurgist a wide field for research of a very fascinating nature. The design of new equipment and the selection and adaptation of materials of construction present some very interesting problems indeed. In the preparation of this paper some of these problems were mentioned briefly but with no attempt to discuss them in detail.

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